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LABORATORY EVALUATION OF CRITICAL FLUID EXTRACTIONS FOR ENVIRONMENTAL APPLICATIONS

by

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16. ABSTRACT The report gives results of a study of the technical feasibility of using critical fluids (condensed gases or supercritical fluids) as extracting solvents to treat oily industrial wastes. The process has the potential for recovering by-product values from the wastes to offset the operating cost of the treatment. Wastes studied at bench-scale were: oily mill scale from the steel industry, oil-laden bleaching clays from specialty- and vegetable-oil decolorization and clarification, and lubricating oil/water waste emulsions from metal working in the aluminum and steel industries. Steel mill scales were successfully de-oiled to below 0.1 wt %, using condensed-gas hydrocarbon and halocarbon solvents for extraction, the recovered oil met acceptable fuel specifications, and credits were sufficient to permit an attractive payout on the investment in treatment equipment. Spent bleaching clays, used to process silicone oils and vegetable (soybean) oil, were treated with hydrocarbon and halocarbon solvents: most of the oil (up to 100%) was recovered, an analyzed silicone oil met product specifications, and the cost of a critical-fluid-based extraction plant of representative capacity would pay out favorably due to credits for recovered oil. Waste lubricating oil emulsions from aluminum-can forming and combined steel mill operations were de-oiled using CO_2 as a solvent near its critical point.

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Industrial Wastes	Decoloring	Stationary Sources		13H
Solvent Extraction	Clarification	Oily Waste	07D	07A
Mill Scale	Emulsions	Critical Fluids	11F	
Clays	Lubricating Oils	Bleaching Clays	11C	
Vegetable Oils	Aluminum Industry	Specialty Oils	11H	
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ABSTRACT

The objective of this program was to determine the technical feasibility of the use of critical fluids (condensed gases or supercritical fluids) as extracting solvents to treat industrial oily wastes. The process has the potential for recovering by-product values from the wastes to offset the operating cost of the treatment. Wastes selected for bench-scale study were:

(1) Oily mill scale from the steel industry;
(2) Oil-laden bleaching clays from specialty oil and vegetable oil decolorization and clarification;
(3) Lubricating oil-water waste emulsions from metal working in the aluminum and steel industry.

Steel mill scales were successfully de-oiled to levels below 0.1 weight percent, using condensed-gas hydrocarbon and halocarbon solvents for extraction. The recovered oil met acceptable fuel specifications. The iron value of the de-oiled scale and the fuel value of the oil would provide sufficient credits to permit an attractive payout on the investment in treatment equipment.

Spent bleaching clays used to process silicone oils and vegetable (soybean) oil were treated with hydrocarbon and halocarbon solvents, and the majority of oil (up to 100%) was recovered. A silicone oil was analyzed and found to meet product specifications. The cost of a critical-fluid-based extraction plant of representative capacity would pay out favorably due to the credits for recovered oil.

Waste lubricating oil emulsions from aluminum can forming and combined steel mill operations were de-oiled using carbon dioxide as a solvent near its critical point.

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I. INTRODUCTION

In recent years, a number of studies have been conducted by the U.S. Environmental Protection Agency for uses of critical-fluid extraction technology for waste treatment. As a solvent extraction, the process has unique advantages in facilitating recovery of by-products and minimizing solvent residues because of the high solvent volatility. Prior studies sponsored by EPA and others have focused on coupling extraction with adsorption: i.e., using critical fluids to strip and regenerate adsorbents which selectively trap organic pollutants from liquid and vapor effluents (1, 2, 3, 4).

More recently, the direct extraction of liquid and solid wastes has been considered. A range of applications of critical-fluid extraction to environmental problems has been considered by Critical Fluid Systems, Inc. From this, three major industrial sectors have emerged as primary areas for further evaluation, according to two criteria: a) magnitude of the environmental problem; and b) economics sufficiently favorable to permit successful introduction of the technology commercially.

Discussions were held with industrial organizations to provide an initial overview of the nature and magnitude of specific pollution problems. Commercial interest was found in a number of areas, and additional information was provided to help define the problems involved. On the basis of these discussions, certain industry areas were proposed to EPA for laboratory testing. These were:

1) Steel-mill oily wastes;
2) Vegetable- and specialty-oil processing wastes;
3) Machining-oil emulsion wastes.

Thus, the objective of this program was to determine the technical feasibility, at bench scale, of the use of critical fluid extraction to treat the above industrial wastes. Also, preliminary information on the economics of this type of process was to be obtained where possible, including the recovery of by-product values.

II. CONCLUSIONS

1. Steel mill scales containing several percent oil can be de-oiled to levels acceptable for sinter-plant feed, using condensed gas solvents such as propane and dichlorodifluoromethane (Solvent-12). Process conditions of ambient temperature and about ten atmospheres of pressure are adequate.

2. The quality of oil extracted from oil mill scale meets acceptable fuel specifications. Heating value, flash point, weight percent combustibles, viscosity, and density are within specifications.

3. A preliminary economic evaluation shows that the credits for de-oiled mill scale and fuel-quality oil provide an attractive payout for a plant de-oiling 90,000 metric tons per year of 5%-oil mill scale feed.

4. Oil-laden spent clays from decolorizing and clarifying silicone oils and soybean oil can be de-oiled using condensed propane and halocarbons such as Solvent-12 and a mixture of Solvent-12 with 1,1-difluoroethane (Solvent 500). Ambient temperature and about ten atmospheres pressure were used.

5. Extracted silicone oil from spent clay met product specifications.

6. Preliminary economics for a plant treating 300,000 lbs/yr (136,000 kg/yr) indicated that a favorable payout could be achieved from recovered oil credits.

7. Waste lubricating-oil emulsions from aluminum can forming were de-oiled using carbon dioxide as an extraction solvent at ambient temperature and about seventy atmospheres. Carbon dioxide broke the emulsion: the treated residue separated into two distinct phases, while the untreated feed did not. Hydrocarbon and halocarbon solvents were unsuccessful because of solvent-feed emulsion formation.

III. RECOMMENDATIONS

1. Testing of both solid and liquid wastes from this study should be extended to a pilot scale sufficient to obtain reliable process data to project to full scale.

2. A broader range of oily solid and liquid wastes from additional industrial sources should be tested for feasibility.

3. Assuming confirming results from pilot-scale program, a full-scale demonstration systems should be built and operated.

IV. THE TECHNOLOGY

A. Fundamentals

The use of near-critical and supercritical fluids as extractants has been of interest for at least 20 years. Successful applications have been developed where the economic gain offsets the cost of high-pressure operations. Two important components of that gain are:

(1) credits from recovery of valuable by-products;
(2) reduced process costs.

Fundamental properties of critical fluids which ultimately lead to such process advantages are reviewed in this section.

The thermodynamic critical temperature is the highest temperature at which two fluid phases (liquid and gas) of a pure substance can coexist. Similarly, the critical pressure is the highest pressure at which two fluid phases of a pure substance can coexist. Table I lists the critical properties for a number of fluids which have been proposed as solvents for extraction processes.

The supercritical fluid (SCF) region can best be visualized with the aid of a reduced pressure-density diagram, shown in Figure 1. The dashed curve is the locus of liquid-vapor equilibrium, which terminates at the critical point (CP). The reduced density of the normal liquid is about 2.6; in other words, the critical density is about 40% of that of the normal liquid (i.e., $1.0/2.6 \cong 40\%$).

The SCF region refers to reduced temperatures in the range of 1 to about 1.4 and reduced pressures from 1 to about 6; the near-critical (NCL) region refers to temperatures near but below $T_r = 1$. In the SCF and NCL regions, fluids still have high enough densities to exhibit liquid-like solubility behavior, yet the densities are low enough so that transport properties are appreciably higher than those of normal liquids.

Studies with solvents such as carbon dioxide, ethylene, and ethane have been reported by a number of investigators (5, 6, 7). As shown in Table I, these three are of interest because they fall in the near-supercritical regime at ambient temperatures, with critical pressures in the range of 50 to 75 atmospheres. In this regime, liquid-like solvent properties are demonstrated, as shown in Figure 2 for naphthalene in CO_2 (8). This diagram is based on published solubility data in the near-supercritical region (7), plus the solubility of naphthalene in saturated liquid CO_2 (9). From these data, two interaction parameters have been derived as required for the Peng-Robinson modification of the Redlich-Kwong equation of state (10), at present the best correlation basis near the critical point.

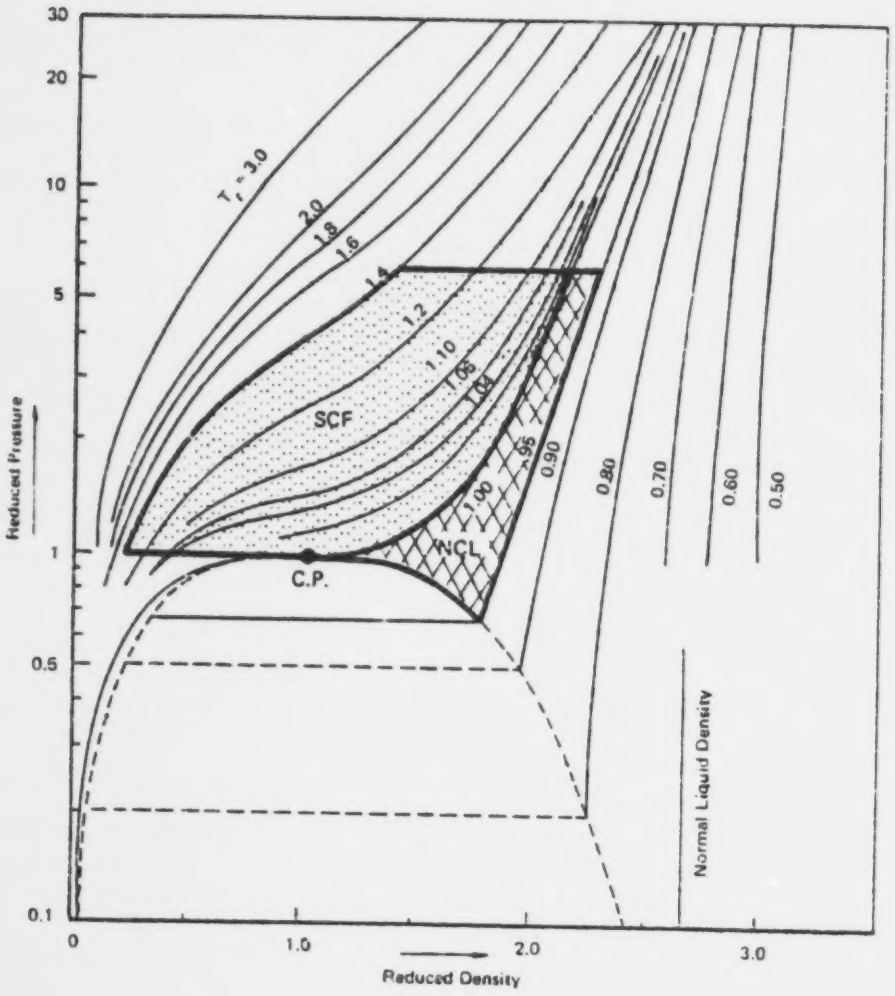

Figure 1. **REDUCED PRESSURE-DENSITY DIAGRAM. SUPERCRITICAL FLUID (SCF) AND NEAR-CRITICAL LIQUID (NCL) REGIONS, AS INDICATED**

NOTE: (reduced function) $x_r = \frac{x_a}{x_c}$

where: x_r = reduced pressure, temperature, density

x_a = actual

x_c = critical

TABLE I

CRITICAL PROPERTIES FOR SELECTED FLUIDS

FLUID	CRITICAL TEMPERATURE (T_c), °C	CRITICAL PRESSURE (P_c), atm	CRITICAL DENSITY (ℓ_c), g/cm^3
Ethane	32.3	48.8	0.203
Propane	96.9	42.6	0.220
Butane	152.0	38.0	0.228
Pentane	296.7	33.8	0.232
Ethylene	9.9	51.2	0.227
Ammonia	132.4	112.8	0.235
Carbon Dioxide	31.1	73.8	0.468
Sulfur Dioxide	157.6	78.8	0.525
Water	374.3	221.1	0.326

Several characteristics of this plot are of interest, and they serve to describe solubility behavior in solvents near the critical point in general. At pressures above 150 atmospheres, the solubility behavior is essentially an extension of that typically observed in the liquid phase: naphthalene solubility increases with increasing temperature, and there is a relatively small effect of increasing pressure. At temperatures above the critical but at pressures below about 80 atmospheres, the "solution" is gas-phase, and the "solubility" of solute is controlled mainly by its vapor pressure. In the intermediate pressure region at supercritical temperatures within 50°C of the critical, there is a mixture of gas-like and liquid-like behavior. Among other phenomena, inversions of solubility trends with temperature at constant pressure are common. The general form of this solubility map is common to all partly-miscible solutes near the critical point of the solvent. The naphthalene-CO_2 data give a good indication of the very large enhancement in solubility that has been observed in solvents that would normally be considered gases, when those solvents are in the near-critical or supercritical state.

Although there are scant data in the literature on solubilities of organic solids and liquids in supercritical fluids, there is a large body of data on solubilities in near-critical liquids (NCL). Francis (9) reported the mutual solubilities of NCL CO_2 at 25°C with each of 261 organic substances. Each of these solubilities represents a single data point on a solubility map. For example, Francis gives the solubility of naphthalene in liquid CO_2 at 25°C as 2 weight-percent. In Figure 2, the corresponding point lies on the saturated liquid curve at 25°C (0.62 mole-percent). Thus, Francis' data can be used as a guide for the magnitude of solubility in the critical region. It should be noted that nearly half of the compounds studied by Francis were completely miscible with NCL CO_2. The naphthalene solubility behavior discussed above is representative of the less-soluble organics in CO_2.

It is evident from Figure 2 that solubility at high pressures (150-300 atm) and supercritical temperatures can be substantially higher than the solubility in saturated liquid at 25°C. At some point of higher pressure and temperature, solutes that are only slightly soluble at 25°C will become completely miscible. That is, the system of solute plus solvent reaches a mixture critical point beyond which only a single homogeneous phase exists. Such critical loci have been reported for a number of organics with CO_2 (11). The pressure-temperature projections of the critical loci for mixtures of CO_2 and several alkanes are shown in Figure 3 (12). For octane, for example, there exists a continuous vapor-liquid (L-G) critical locus connecting the critical points of the pure materials. There is also a liquid-liquid (L-L) critical locus that exists at low temperatures. To the right of the L-L critical and above the L-G critical, only one phase exists; in that region, octane and CO_2 are completely miscible. For tridecane and higher molecular weight alkanes, the L-G and L-L critical loci merge into a single continuous critical locus. To the upper right side of the critical locus, the system is completely miscible; below it and to the left, the system exhibits two or more phases of limited miscibility.

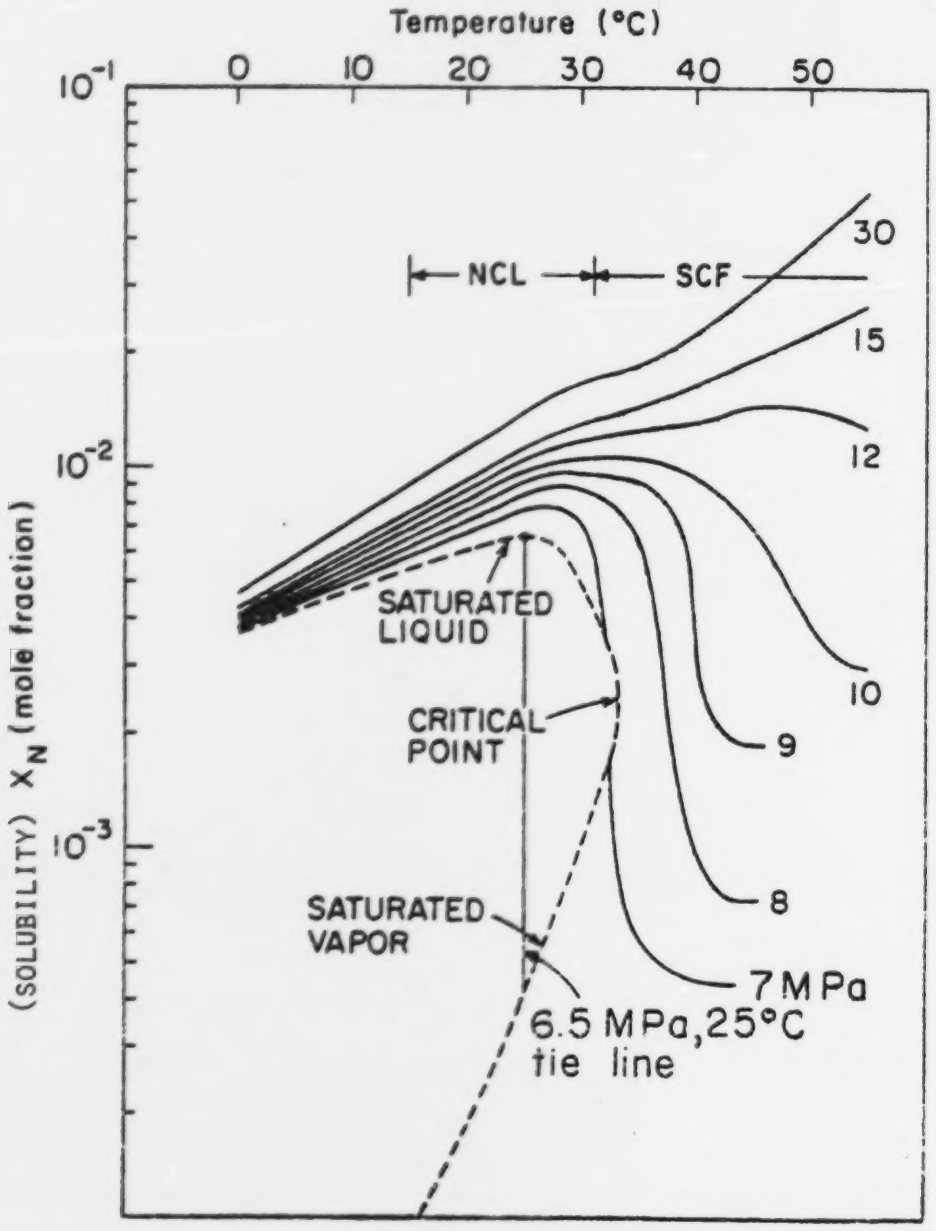

Figure 2. SOLUBILITY MAP OF NAPHTHALENE IN SCF AND NCL CARBON DIOXIDE

1 atm. = .1013 MPa

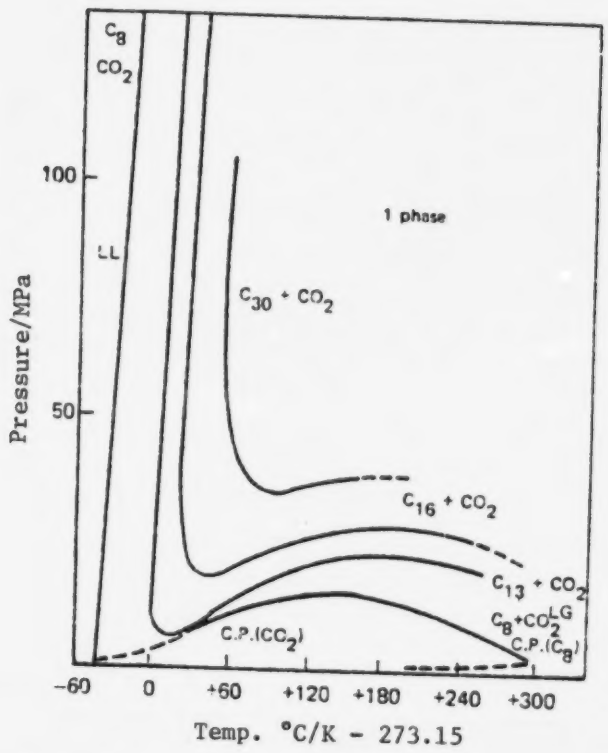

Figure 3. P–T PROJECTIONS OF THE PHASE DIAGRAMS AND CRITICAL LOCI OF BINARY CO_2 + ALKANE MIXTURES. FULL LINES, CRITICAL CURVES; HATCHED LINES, VAPOR PRESSURE CURVES OF CARBON DIOXIDE AND OCTANE, RESPECTIVELY.

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This brief discussion of solubility phenomena in the critical region illustrates several important generalizations:

1. Enhanced solubility in the critical region is a general phenomenon exhibited by any solute.

2. A large number and variety of organic compounds are partially or completely miscible with CO_2 in the near-critical liquid region. Similar behavior has been shown for other non-polar solvents.

3. Partially miscible systems at near-critical liquid conditions tend toward complete miscibility at supercritical conditions.

In addition to high solubility, a good extracting agent should exhibit high diffusivity for rapid mass transfer. There is relatively little direct data on diffusivities in supercritical fluids, but there is a growing body of indirect evidence showing rapid mass transfer.

Several investigators have measured self-diffusivity of CO_2 in the sub- and supercritical region (13). These data have been correlated to develop a map of self-diffusivity as given in Figure 4. In liquid CO_2 at 25°C, the diffusivity is about an order-of-magnitude higher than that of conventional liquid solvents. The vapor diffusivity at 25°C is higher by another factor of 10. At supercritical temperatures, the diffusivities vary between 10^{-3} and 10^{-4} cm^2/sec, decreasing from the higher to lower values with increasing density. By comparison of Figures 2 and 4, it can be seen that the decrease in diffusivity with density is less than the increase in solubility with density. For example, at 40°C the diffusivity decreases from 7×10^{-4} cm^2/sec at 80 atm to 1.5×10^{-4} cm^2/sec at 120 atm, by a factor of 4.7, while the solubility increases from 80 atm (0.1 mole-percent) to 120 atm (1.2 mole-percent) by a factor of 12. Thus, the gain in solubility at higher density more than outweighs the decrease in diffusivity.

Further evidence of favorable transport properties come from viscosity of CO_2 around the critical point. Figure 5 gives viscosity data in the temperature and pressure range of interest (14). Values are on the order of 0.04-0.08 centipoises, about a factor of 10 to 20 lower than those of normal liquids.

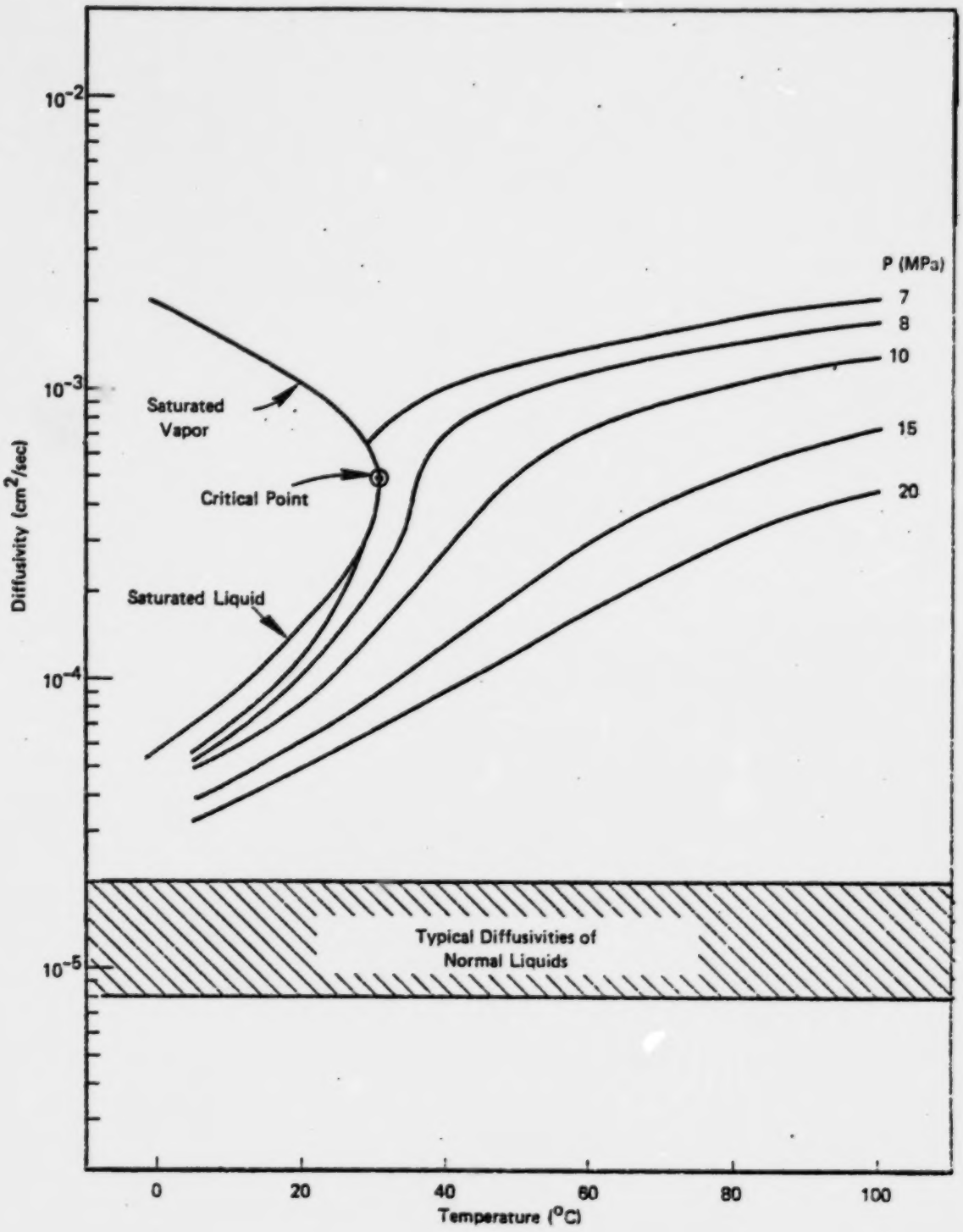

Figure 4. DIFFUSIVITY OF CARBON DIOXIDE IN THE SCF AND NCL REGIONS

1 atm. = 0.1013 MPa

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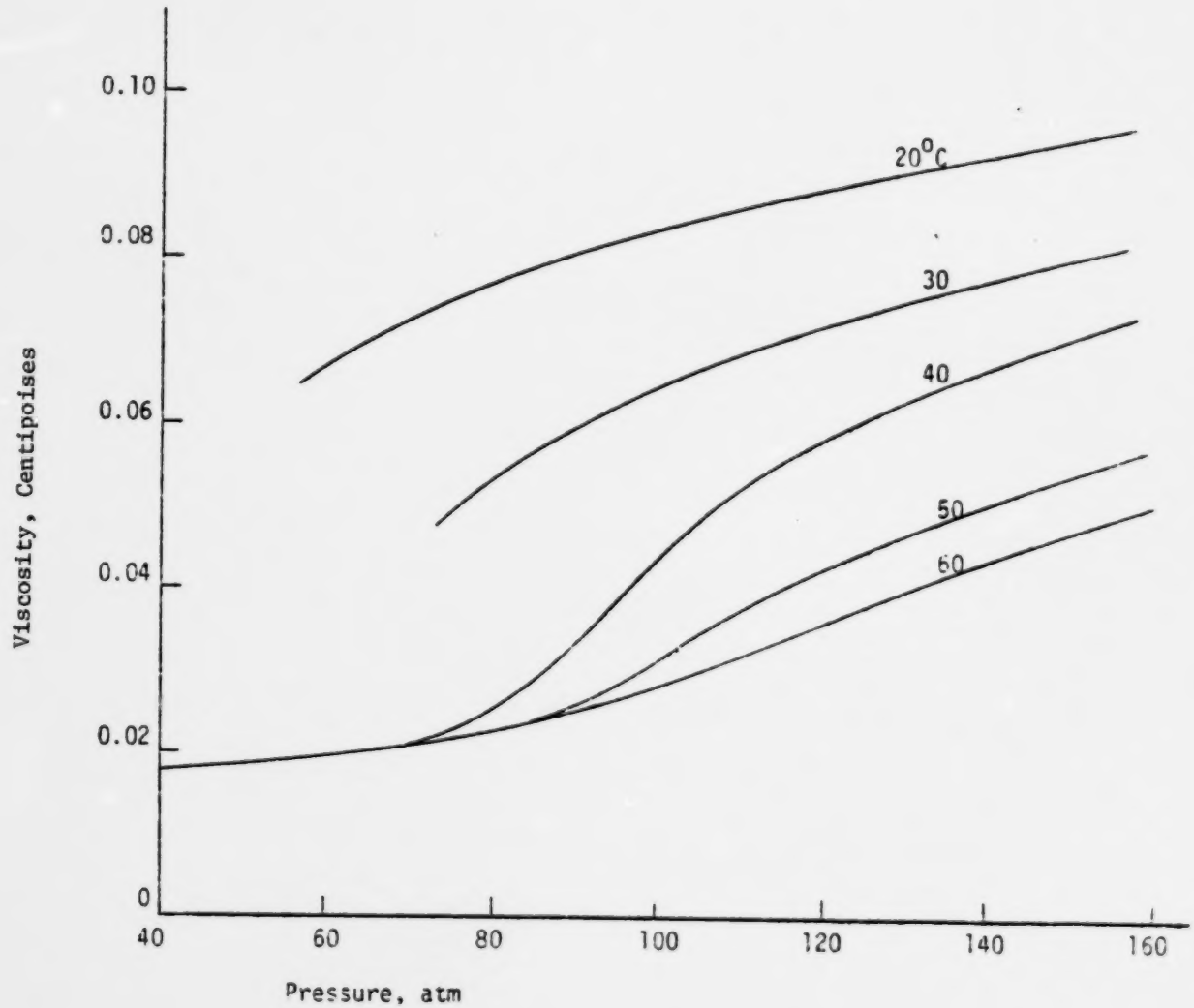
Figure 5

Viscosity of Carbon Dioxide



Certain unusual thermophysical properties of fluids near the critical point have implications in process engineering. The latent heat of vaporization at the critical point is zero, because of the disappearance of the phase transition. As saturation temperature-pressure conditions for vapor-liquid equilibrium approach the critical point, the heat of vaporization decreases rapidly; this change is illustrated in Table II (15), showing the latent heat for carbon dioxide near its critical point. At 0°F (-17.8°C), the value is about 120 btu/lb (216 cal/gm); at 70°F (21.1°C), it is about half, 64 btu/lb (115 cal/gm).

A second anomalous aspect of thermophysical behavior is related to heat capacity in the supercritical regime (16). At temperatures about 15-20°C above the critical, heat capacities are unusually high, several-fold higher than the liquid value. At 1-2°C above the critical, the heat capacity is about an order-of-magnitude higher than the corresponding liquid value.

TABLE II

HEAT OF VAPORIZATION OF CARBON DIOXIDE

Temperature (°F)	Temperature (°C)	Saturation Pressure (atm)	Heat of Vaporization (btu/lb)	Heat of Vaporization (cal/g)
0	-17.8	20.8	120.1	(66.7)
40	4.4	38.6	95.0	(52.8)
60	15.6	50.9	76.6	(42.6)
70	21.1	58.1	63.8	(35.4)
80	26.7	65.9	44.8	(24.9)
87.8	31.0	72.7	0	(0)

V. MILL SCALE DE-OILING

A. Nature of the Problem

The steel industry represents a major producer of oil-containing solid wastes. While a broad range of scale and sludges are produced, the major volume problem is mill scale. Mill scale is waste iron oxides, partly contaminated with lubricating oils, scraped from the surfaces of formed steel such as rolling stock. Table III provides a summary of the major oil-bearing wastes from steel plants. The tonnage levels shown are estimated ranges for a 2.5 million metric-ton-per-year steel plant.

Mill scale amounts to 4% to 5% of the total raw steel production. Its oil content is varied, but can run as high as several percent for the composite scale for a total mill, and much higher for certain specific operations. A 1978 study (17) showed that about half the mill scale produced is recycled to sinter plants for return to the blast furnace; the other half is stockpiled. The study also showed that about 11% of all lubricants purchased by steel mills ultimately becomes the oil fraction of mill scale.

Coarse mill scale (>5mm) has a low oil content (18) and may be recycled as a direct metallic charge to the blast furnace. Mill scale fines (<5mm), which are 80% to 85% of the total mill scale, have an oil content sufficiently high to adversely effect sinter plant operations. The oil is volatilized during sintering and recondenses in the sinter-plant off-gas. Without treatment, the gaseous effluent can produce a visible plume; where bag houses are used, the oil can condense and impair the operation.

Several de-oiling methods have been tested. Water washing using hot alkaline solution can remove the majority of oil on mill-scale fines. The method has the advantage of low cost. However, at best, 5% to 10% of the initial oil remains on the mill scale. Thermal incineration methods have been tested, and a direct-fired kiln has been reported in commercial use (18). The principal advantage of incineration is high percentage removal of oil. The major disadvantage is high fuel cost, which includes treatment of the kiln off-gas by after-burning. Consideration has been given to the use of liquid solvent washing, in which a chlorinated hydrocarbon solvent is used to extract the oil from mill scale fines, and then distilled to recover the solvent. While no details are available, this method would seem to have the advantage of recovering the oil fraction for use as fuel, or even for recycle as a lubricant. Energy costs for solvent distillation may be high, and residual solvent on the de-oiled fines would have to be evaluated.

TABLE III

IRON-CONTAINING SOLID WASTES GENERATED IN THE STEEL PLANTS

	Hydrocarbon Content (%)	Iron Content (%)	Water Content (%)	Contaminants	Tonnage* (TPY)
Sinter Plant Scrubber Sludge	0-2	20-40	2-40	Alkalies, Zn, Pb	400-500
Mill Scale	0.01->1	60-75	2-5	---	37,500 - 250,000
Scarfer Scale	0.01-0.5	70-85	5-10	---	30,000 - 60,000
Hot Rolling Mill Sludges	5-30	60-70	21-58	---	2,000 - 4,000
Cold Mill Sludges	2-7	---	81-88	Zn, Sn	5,000 - 7,000
Centerless Grindings	---	60-85	---	---	2,500
Waste Water Treatment Sludges	2-8	0-44	40-78	P, Zn, Cr, Sn	7,000 - 20,000
Creek Dredge Spoil	Neg.-2	Neg.-40	30-50	SiO_2, Al_2O_3, S	Neg.- 5,000

*Based on a nominal 2.5 MTPY steel plant.

After evaluation of other processes, it appeared that an economical solvent washing process might be feasible, based on condensed gases or supercritical fluids as solvents. Energy costs for such processes are known to be low (20), and solvent residues are virtually zero. The process would accomplish three objectives:

(a) elimination of an oily waste;
(b) recovery of the iron values in the scale for recycle;
(c) recovery of this oil values, probably at fuel value.

B. Experimental Studies

1. Extraction Apparatus and Procedures

A bench-scale experimental study of mill scale de-oiling was conducted to determine the basic technical feasibility of using critical-fluid solvents. These data were then used to support estimates for both capital and operating costs of the process.

The experimental systems used for extractions are sketched in Figures 6 and 7. Figure 6 shows the apparatus used for small-scale extractions, employing a vessel of 1.59 cm (0.625 in) diameter and 30.5 cm (12 in) length. Figure 7 shows the apparatus used for larger-scale extractions, with a vessel of 3.18 cm (1.25 in) diameter and 152 cm (60 in) length.

For extractions at ambient temperature, the procedure was to load the extractor with oily mill-scale feed and connect it to the system. The system was pressurized with solvent and then a constant flow was introduced using a diaphragm compressor or pump. Flow rates, initial and final weights, pressures, and temperatures were monitored and recorded. For small-scale runs, extract collection tubes (U-tubes) were changed after sufficient sample was obtained in each. The extraction was concluded when no additional oil was visually observed in a U-tube. The system was then depressurized and the extractor disconnected to unload the residue of de-oiled mill scale.

For larger scale extractions, oil samples were collected by discharging oil from a sight gauge used as the two-phase separator. Discharged oil samples were weighed and solvent volumes recorded to give an extraction curve.

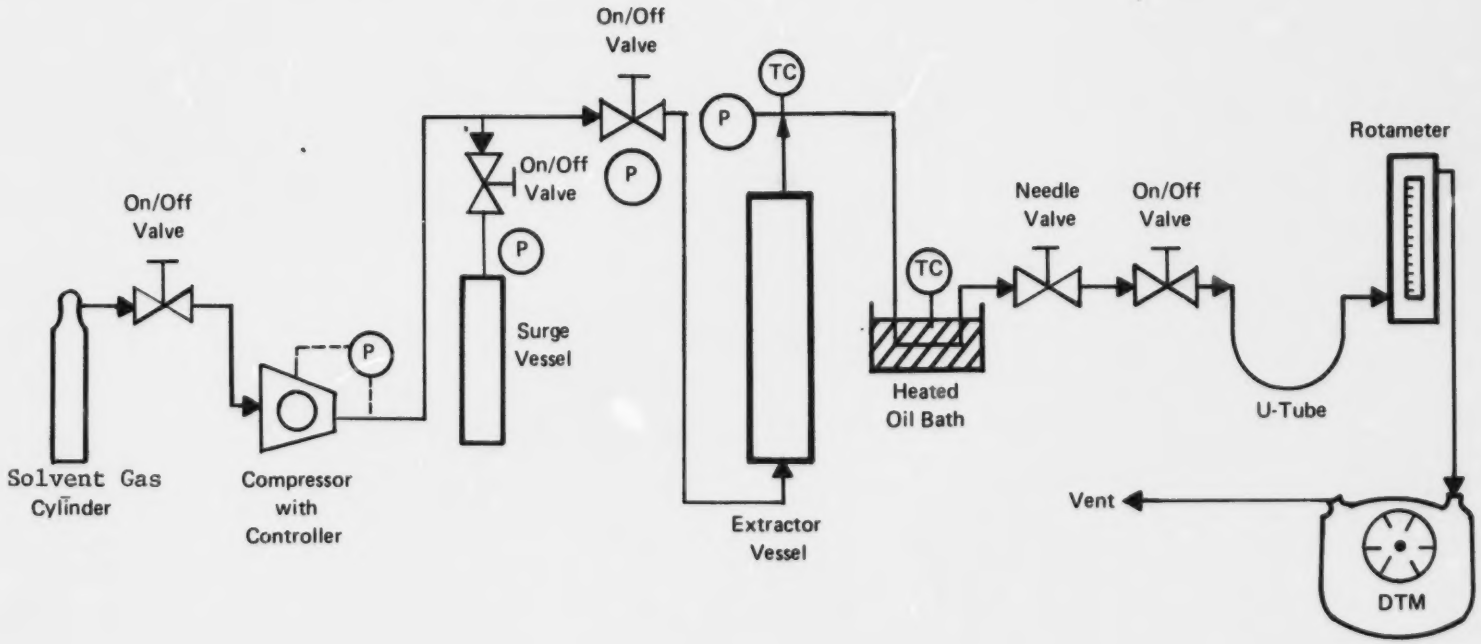


FIGURE 6: SMALL-SCALE EXTRACTION APPARATUS

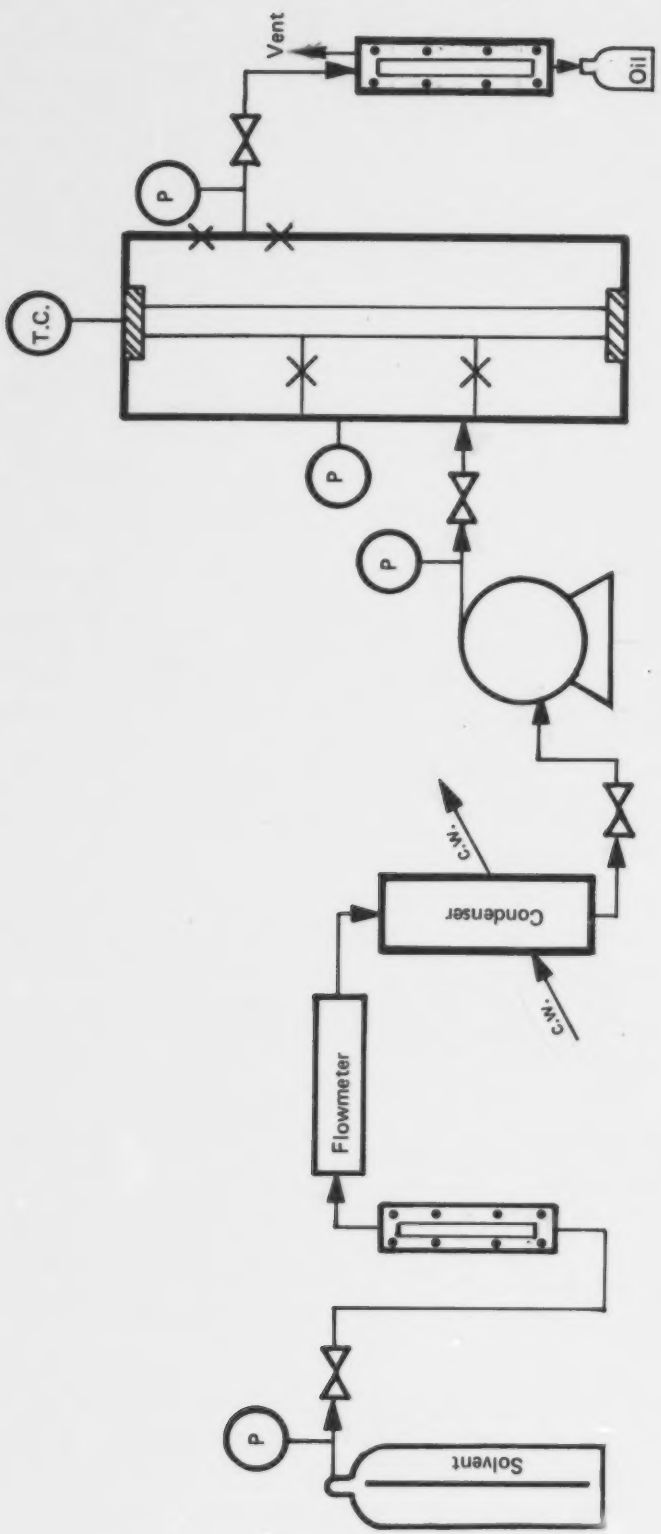


FIGURE 7: KILOGRAM-SCALE EXTRACTION APPARATUS

C. Experimental Data

1. Carbon Dioxide as a Solvent

An initial comparative series of runs was made to provide data on the relative effectiveness of carbon dioxide as a solvent. Solvents typically considered for oil extractions include:

(a) Carbon Dioxide. CO_2 is potentially attractive in any extraction process because it is inexpensive (about \$0.04/lb), chemically inert and thus safe for use in processing, and readily available. As a process solvent in a condensed state it has two principal disadvantages: high pressures are needed to render it useful as a solvent (greater than 65 atm at room temperature and above), and relatively poor solubilities of heavier oils.

(b) Propane. Propane has the advantages of low operating pressures to maintain a condensed phase (10-20 atm), and good solubilities including complete miscibility for many hydrocarbon solutes. Its cost is moderate, about \$0.20/lb, but it has the disadvantage of requiring special design and processing procedures because of its flammability.

(c) Chlorofluorocarbons. These materials, such as dichlorodifluoromethane (Solvent-12) also can be maintained in a condensed state at low pressures (10-20 atm), where they have good hydrocarbon solubility. Their costs are greater, the lowest being about \$0.70/lb for Solvent-12. They are chemically inert at low temperatures, and have no flammability problems.

Prior experience has indicated that hydrocarbon and halocarbon solvents behave similarly. Thus, only one of these, propane, was chosen for comparison with CO_2. A composite mill scale sample of 1.0% oil content was used. The experimental runs were carried out until little or no further oil extraction could be observed, and the amount of solvent per unit of feed weight was noted. This parameter determines the relative effectiveness of the solvent. The results are summarized in Table IV.

Propane extractions were carried out at about 50 atm and room temperature. This high pressure was maintained to assure that the solvent would remain condensed in the experimental system, because pressure fluctuations occur due to pump cycling, and the solution is sometimes heated to prevent oil precipitation in the small-diameter lines and valves. Virtually complete oil removal was achieved with a solvent-to-mill scale ratio of 1.4 by weight.

TABLE IV

COMPARISON OF CO_2 AND PROPANE FOR MILL-SCALE DE-OILING

SOLVENT	PRESSURE (psia)	TEMP. (°F)	SOLVENT/ FEED WEIGHT RATIO	FEED WT% OIL	% OF FEED EXT. AS OIL
Propane	700	75	1.4	1.0	1.0
Carbon Dioxide	2200	120	17.0	1.0	0.9

Carbon dioxide was run at 150 atm and 50°C, with a final solvent/feed ratio of 17. Even at this high solvent use, there was incomplete oil removal.

Thus, from these comparative tests, it was concluded that further work with CO_2 would not be worthwhile.

2. Propane and Dichlorofluoromethane as Solvents: Small Scale Tests

A second test series was carried out with mill scales from three different sources, each run with propane and with Solvent-12 (dichlorofluoromethane) as solvents.

All mill scale samples used in this series were taken from stockpiled composite sources. After discussions with steel mill personnel, it was concluded that these would be most representative of materials that required de-oiling prior to sintering, in contrast to segregating from specific operations. At least two source mills provided samples that were drawn from the bottom of settling lagoons.

Oily mill scale feeds for these tests were screened to provide a particle-size analysis, and the individual screened segments were analyzed for oil in most cases, using Soxhlet extraction. These results are summarized in Table V. As shown, the full-range samples have oil contents ranging from 0.4 to 1.0% oil. The distribution of oil as a function of particle size is inconsistent. Sample B shows an expected distribution if oil content were related to surface area: larger particles have less surface, and thus less surface oil. This trend does not hold for Samples A & C, however; this may be related to differences in particle shape factors for different particle sizes.

The results of extraction tests are summarized in Table VI. Extraction curves are shown in Figures 8, 9, and 10.

TABLE V

SOXHLET AND SIEVE ANALYSIS ON FEEDS, WT %

	FULL SAMPLE	STANDARD MESH SIZE			
		-40	+40-16	+16-8	+8
MILL SCALE					
A.					
%, by weight of total	100	1	31	56	12
Oil Content, wt %	0.97	--	0.68	0.70	1.08
B.					
%, by weight of total	100	1	42	29	28
Oil Content, wt %*	0.96	1.23	1.18	.65	.55
C.					
%, by weight of total	100	1	22	28	49
Oil Content, wt %*	0.43	--	0.12	0.26	0.13

*Single samples.

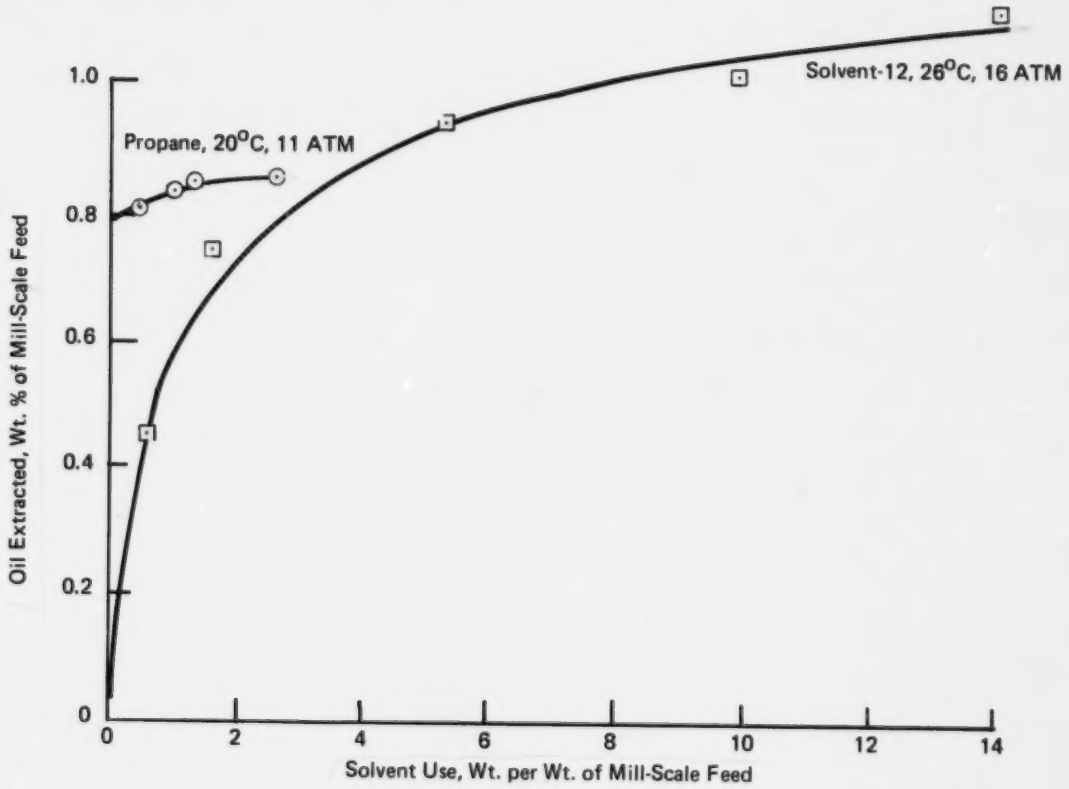


FIGURE 8 EXTRACTION CURVES: SMALL-SCALE SERIES MILL SCALE B

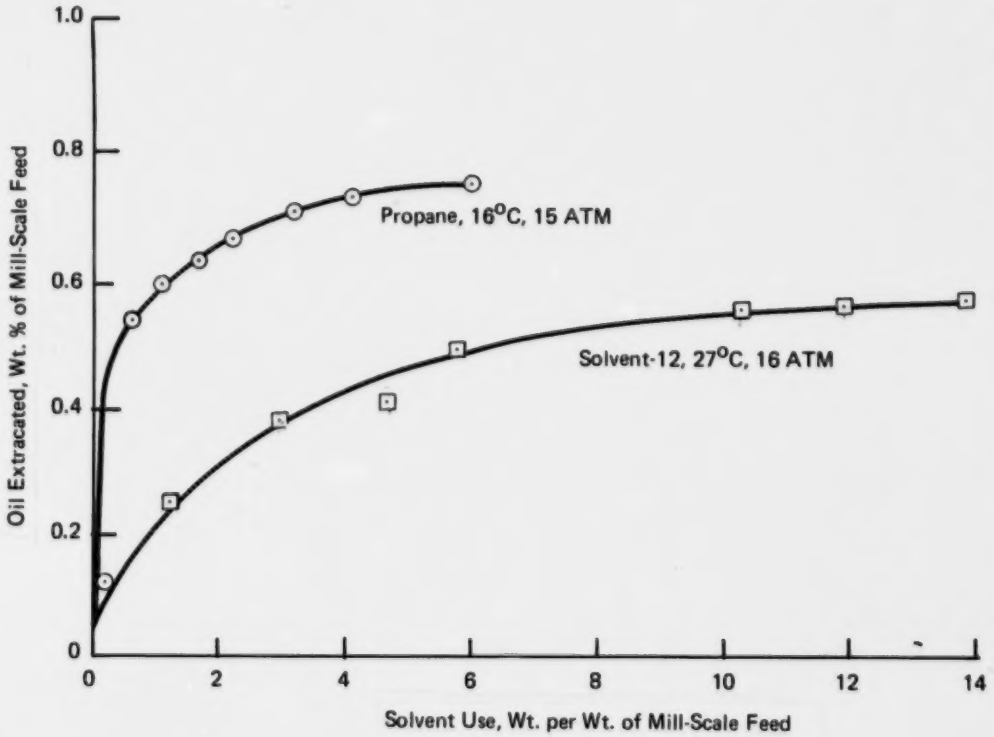


FIGURE 9 EXTRACTION CURVES: SMALL-SCALE SERIES MILL SCALE A

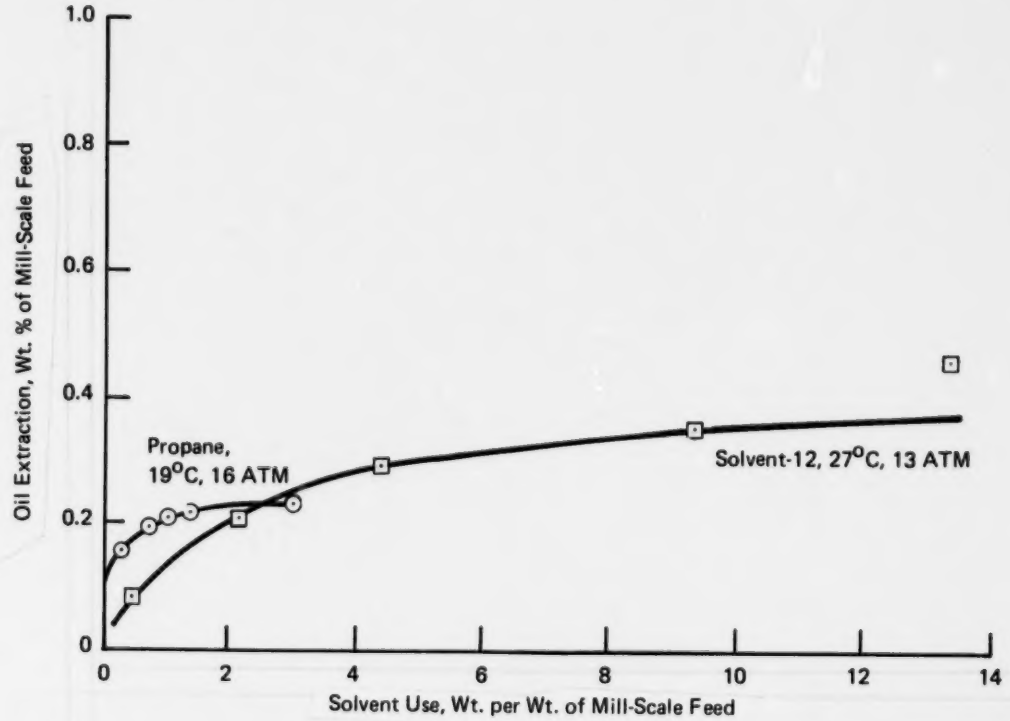


FIGURE 10 EXTRACTION CURVES: SMALL-SCALE SERIES MILL SCALE C

In Table VI, the quantity of oil collected can be compared to that measured in the feed, to give an indication of the success of de-oiling in a given run. Oil analyses of the residues are less reliable because of inaccuracies in the soxhlet extractions at low oil contents. Also, inhomogeneities in the oil content of the solid make it difficult to obtain representative samples for analysis. Unfortunately, this was also a problem for feed samples, as well. These considerations are discussed in Appendix A, Quality Control Evaluation Report. In general, most mill scale samples were relatively dry (<10%), and the collected oil may have contained small amounts of water which were difficult to detect because of the murky appearance of oil extract samples.

Runs 2-5 gave oil collection efficiencies of about 80-120%. Runs 1 and 6 gave lower figures (55 and 60%). Because of the relatively large quantities of solvent used, it is probable that essentially complete oil removal occurred in each run. Figures below 100% may have been due to incomplete collection of extracted oil in the sample tube, and/or a feed oil content actually below the as-analyzed value (see Appendix A).

Table VII gives residual oil contents by Soxhlet analyses, where residual oil is defined as the oil left on the mill scale after extraction. While the reliability is questionable at these low oil levels (see Appendix A), the results show 80-100% oil removal, in confirmation of the oil-collection data.

Bed compression occurred in all runs where measured, and high pressure drop for solvent flow was noted in some cases. Oily solids with a wide range of particle sizes have been found to show plugging tendencies when flow is introduced rapidly. If pressurization occurs slowly, compaction of the bed is normally less severe.

The relative effectiveness of propane vs. Solvent-12 is shown in the comparative extraction curves for each mill scale (Figures 8-10). In general, propane appeared to be more efficient in each case, although Solvent-12 also was capable of de-oiling the samples. Quantitative comparison was not possible at this point, due to the small beds used, and the imprecision of the data as discussed above.

TABLE VI

SUMMARY OF MILL SCALE RUNS IN SMALL VESSELS

MILL SCALE FEED MILL SCALE FEED	RUN # 1	RUN # 2	RUN # 3	RUN # 4	RUN # 5	RUN # 6
Mill Scale	A	A	B	B	C	C
Solvent	Solvent-12	Propane	Solvent-12	Propane	Solvent-12	Propane
Temperature (°C)	27	16	26	20	27	19
Pressure (atm)	8-21	8-25	8-25	11	12-15	11-21
Feed Weight (g)	84.64	219.59	102.53	325.0	118.73	338.58
Feed Bulk Density (g/cc)	1.84	1.82	2.69	2.80	2.47	2.81
Residue Weight (g)	81.32	195.59	100.14	317.58	117.9	334.91
Residue Bulk Density (g/cc)	1.98	1.46	3.06	3.26	2.75	---
Total Oil Collected (g)	0.49	1.69	1.17	2.79	0.61	0.80
Total Solvent Used (g)	1179.13	1313.10	1885.18	869.04	2792.97	1031.58
Oil in Feed[1] (g)	0.82	2.13	0.98	3.12	0.51	1.46
Collection Efficiency[2] (%)	59.7	79.3	119.4	89.4	119.6	54.8
Velocity thru Bed (cm/sec)	---	---	---	0.02-0.17	0.1-0.3	0.1-0.28
Bed Compression	2.3/21.5=	2.5/33=	2.5/17.8=	5/30=	2.5/22.5=	---
(cm/initial cm of bed)	11%	7.6%	14%	17%	11%	---

[1]Based on soxhlet extraction (see Table V)

[2]Based on [(Collected Oil) ÷ (Oil in Feed)]

TABLE VII

Soxhlet Analysis* of the Mill Scale Feed and the Extracted Residue

MILL SCALE	SOLVENT	FEED OIL % BY FLASK WEIGHT GAIN	RESIDUE OIL % BY FLASK WEIGHT GAIN
A	Solvent-12	0.97	0.2044
	Propane	0.97	0.13
B	Solvent-12	0.96	0.08
	Propane	0.96	0.16-0.0225
C	Solvent-12	0.43	0-0.1324
	Propane	0.43	0.09-0.1751

*Based on single samples.

3. Propane and Dichlorodifluoromethane As Solvents: Kilograms-Scale Tests

Additional extraction tests were carried out in a larger column, 3.18 cm in diameter and 152 cm (5 ft) in length. These kilogram-scale tests served several purposes. First, as the extract solution flows through the column and builds up oil concentration, its viscosity increases, and potential column plugging problems may become apparent; there is a greater chance that the problem would be manifested in the longer column. Second, the larger diameter mitigates flow channeling due to wall effects that might be exaggerated in the small-scale column work. Third, larger and thus more accurate weights of samples can be obtained, which improves the definition of the extraction curve.

Three such tests were carried out: one using propane with mill scale B as feed (Figure 11), and two with mill scale C, using propane in one and Solvent-12 in the other (Figure 12).

The curves consistently level out at oil extractions below those determined in the small-scale runs (dashed curves in Figures 11 and 12). This may be due to poorer laboratory separatory efficiency at the higher solvent flow rates, causing some of the extracted oil to escape with solvent from the separator. Otherwise, there seems to be reasonable correspondence between small-scale and kilogram scale; the two sets utilized mill-scale charge weights which were different by a factor of ten or more.

As with the small-scale runs, it is difficult to determine the degree of de-oiling with accuracy. As shown in the summary in Table VIII, both solvent runs with mill scale C showed low levels of de-oiling. This may be due to an inherent difficulty in processing this mill scale. Alternatively, it may be that feed analyses are inaccurate in representing the oil levels of the samples used. The Soxhlet analyses of necessity are done on small samples, and accurate numbers may not be obtainable without analyses of a large number of feed aliquots.

TABLE VIII

SUMMARY OF KILOGRAM-SCALE RUNS

Mill Scale	B	C	C
Solvent	Propane	Propane	Solvent-12
Temperature (°C)	19	15	13
Pressure (atm)	11	11	11
Feed Weight (g)	3115.60	2964.62	2961.78
Total Oil Collected (g)	22.93	4.75	3.59
Residue (g)	3025.28	2811.41	2855.60
Total Solvent Used (g)	1023.5	1370.0	3402.1
% Oil in Feed (by Soxhlet Analysis)	0.97	0.43	0.43
Oil in Feed (g)	30.22	12.75	17.74
Bulk Density (g/cc)	2.74	2.60	2.60
Collection Efficiency[1] (%)	76	37	28

[1]Based on [(Oil Collected) / (Oil in Feed)]

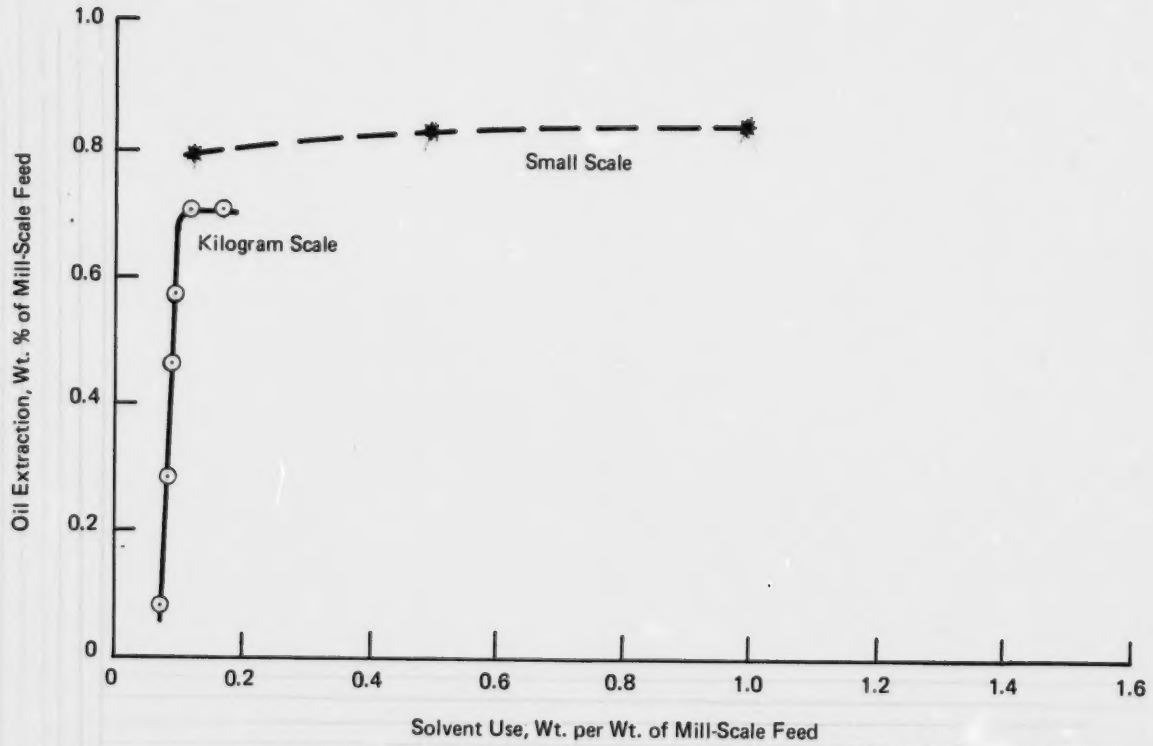


FIGURE 11 EXTRACTION CURVES: KILOGRAM SCALE MILL SCALE B PROPANE

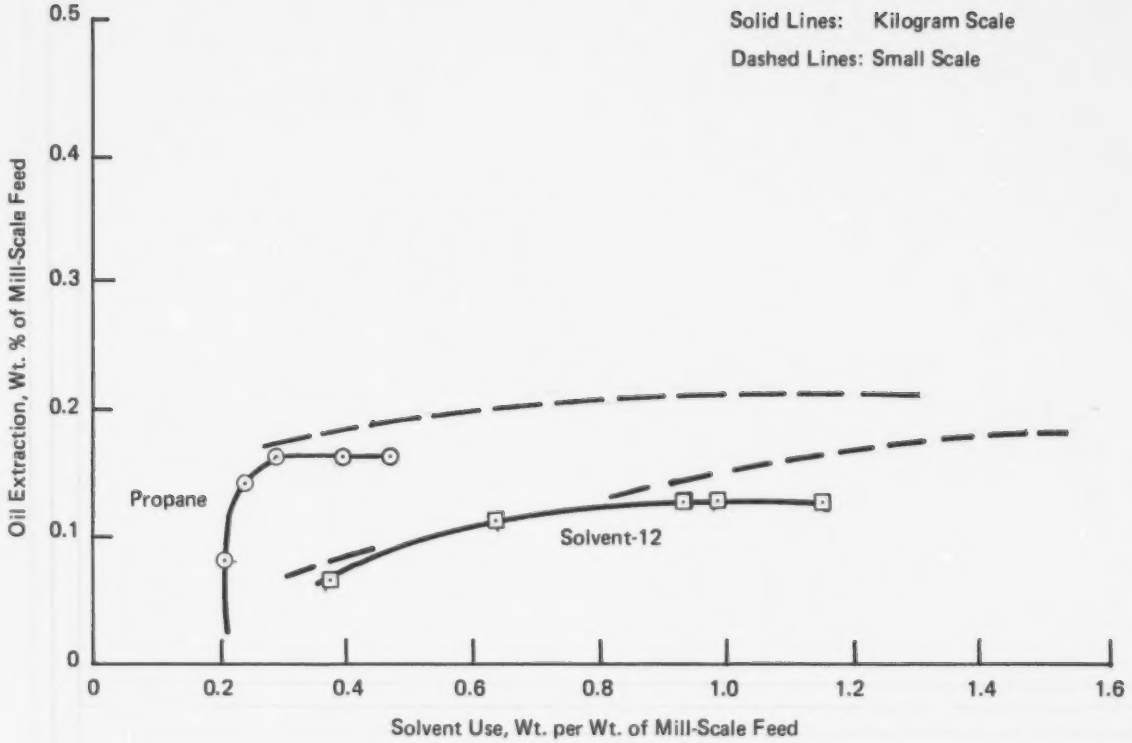


FIGURE 12 EXTRACTION CURVES: KILOGRAM SCALE MILL SCALE C

4. Quality of Extracted Oil

The recovery of oil for fuel value is a potential credit for a mill scale de-oiling process. Because of the compositing of various steel mill oily wastes, there is little chance of recovering oil of lubricating-oil value. However, at mid-1983 fuel-oil prices of about $0.60 per gallon, oil recovery for fuel is significant in itself.

A separate mill scale sample (mill scale D) was processed to obtain an extracted oil volume sufficient for analysis. The sample had a feed oil content of 7.5%, and the residue after extraction with Solvent-12 had an oil content of 5.3%. The sample had a high water content, 26.1%, and this may have accounted for a somewhat greater difficulty in de-oiling than experienced with samples A, B, and C.

Oil analyses are summarized in Table IX. Heating value was 19,000 Btu/lb, and combustibles were 96.4%. Flash point was >260°C (the latter being the temperature at which the sample began to flare). Staff from the sample source steel mill indicated that the oil had acceptable fuel characteristics.

D. Mill Scale De-Oiling Plant Process Design and Economics

A preliminary design was prepared for a mill scale de-oiling plant for the purpose of a process feasibility study. Solvent-12 was selected for the design study. Even though propane showed more favorable extraction characteristics, it was felt that solvent-12 would be acceptable for a broader range of sites. Propane would be disadvantageous at locations where the normal precautionary design and operating procedures that accompany a potentially flammable solvent might be difficult or costly.

The plant is capable of processing 90,000 metric tons per year, or 12.5 tons per hour of mill scale (oil-free and dry-basis). Oil content is 5.0%. Design criteria are summarized in Table X. Cost figures are presented in Table XI. Equipment costs are listed in Table XII, and total capital costs are given in Table XIII. Summarized below are the results of this study:

(a) A capital investment of $1.75 million is an "order of magnitude" estimate for the de-oiling plant.

(b) An operating cost of $0.5 million per year, or $5.67 per ton mill scale is estimated.

(c) Based on the value of the recovered oil @ 60¢/gallon and the de-oiled mill scale @ $12/ton, the de-oiling plant would yield a net profit of $1.48 million per year. The payout time for the $1.75 million investment is about 15 months.

TABLE IX

ANALYSIS OF OIL EXTRACTED FROM MILL SCALE

Property	Value	Source of Analysis
Elemental Analysis:		
Carbon	86.16%	(1)
Hydrogen	12.42%	
Nitrogen	0.05%	
Sulfur	0.78%	
Thermal Gravametric Analysis (TGA):		(2)
Moisture and Volatile Organics	1.2%	
Combustibles - Liquids and Solids	96.4%	
Ash (600°C)	2.4%	
Density, 22°C	0.915 g/ml	(2)
Viscosity	390 cp	(2)
Flashpoint	>260°C	(2)
Heating Value	19,227 Btu/lb.	(1)

SOURCES: (1) Galbraith Laboratories, Knoxville, TN
(2) Arthur D. Little, Inc., Cambridge, MA

TABLE X

MILL SCALE DE-OILING PLANT DESIGN CRITERIA

• FEED CONDITIONS	Temp.:	50-100°F(10-38°C)
	Oil Content:	3-6%
	Moisture:	5-10%
	Particle Size:	-325 to +4 mesh
• PRODUCT QUALITY	Oil Content:	<0.1%
	Moisture:	5-10%
• PRODUCT RECOVERY	Oil:	<98%
	Iron plus Iron Oxide:	<99%
• SOLVENT RECOVERY	99.98%	
• PLANT CAPACITY	90,000 Tons Per Year	
• EXTRACTION TEMPERATURE/ PRESSURE	70-80°F/100-120 psia (21-27°C/7-8 atm)	

TABLE XI

OPERATING COST FOR MILL SCALE PLANT*

(Basis: 90,000 Tons Per Year De-Oiled Mill Scale)

	ANNUAL COST
LABOR: 1 Operator per shift @ $24/hr	$ 210,240
SUPERVISION: ¼ Supervisor @ $36/hr (day shift only)	26,280
ELECTRICITY: 2.3×10^6 kw-hr/yr @ 5¢/kw-hr	115,000
COOLING WATER:	
Water: 11×10^6 gallons/yr @ 22¢/1,000 gal.	2,420
SOLVENT:	
Solvent Make-Up: 72,000 lbs/yr @ $0.70/lb	50,400
MAINTENANCE Cost @ 4% of Capital Investment	70,000
TAXES and INSURANCE @ 2% of Capital Investment	35,000
	$ 509,340
CREDIT ON RECOVERED OIL	
(1.5×10^6 Gallons @ 60¢/gallon)	($900,000)
CREDIT ON RECOVERED MILL SCALE	
(90,000 Tons @ $12/Ton)	($1,080,000)
NET PROFIT	$1,470,660
PAYOUT TIME (for $1,752,400 Capital)	One Year, Three Months

*Actual local costs and credits for specific plant site location studied.

TABLE XII

MILL SCALE DE-OILING PLANT

EQUIPMENT COSTS

Extraction Columns (2)	$100,000
Compressors:	
200 HP	125,000
25 HP	50,000
Solvent Stripper	20,000
Heat Exchangers	88,000
Decanter, Flash, & Separator Drums (6)	56,000
Pumps (4)	18,000
Tanks/Bins (2)	20,000
Solids Conveyors (3)	15,000
	$492,000

TABLE XIII

MILL SCALE DE-OILING PLANT*

CAPITAL COST

DESCRIPTION	TOTAL $
Civil and Structural Work	98,400
Auxiliary Construction Work	72,000
Lab Equipment and Furniture	20,000
Plant Equipment	492,000
Plant Piping	133,000
Offsite Piping	20,000
Electrical	74,000
Instrumentation	123,000
Installation Costs	350,000
Engineering	200,000
Expense Items	20,000
Contingencies	150,000
	1,752,400

*Engineering or order of magnitude estimates.

VI. DE-OILING OF BLEACHING CLAYS

A. Nature of the Problem

The refining of certain synthetic and natural oils includes a processing step to decolorize, or bleach, the refined product using special clays. Specialty oils treated in this way include high-value fluids such as silicones. Also, a large volume of crude vegetable oils, such as soybean, corn, cottonseed, peanut, and sunflower are bleached with clays. The clay is mixed with the oil, and the spent clay is filtered from the clarified oil. The resulting clay filter cake contains about 30-60% occluded oil, and thus represents a pollution problem as well as a yield loss. About 0.5 pounds of clay is used per 100 pounds of refined oil product in vegetable oil treating.

Spent oily clay is a solid waste with typical disposal problems, plus some special problems and opportunities in some cases. By extracting oil and thus separating it from clay, normal hauling costs for solid waste disposal would be reduced, at least by the fractional removal of oil. In fact, reductions of oil content of the waste could allow disposal in a lower-class landfill, and reduce the cost per unit weight as well. At the same time, there is the potential for recovery of the oil product for blending with either refined or crude product oil. There may also be a potential for recovery of clay for reuse, inasmuch as clay activity may not be entirely spent each cycle. Finally, in the case of vegetable oils, the hazard of spontaneous combustion of stored oil clay would be eliminated. At present, combustion is inhibited by adding water, which adds to the estimated waste disposal cost.

Data on the quantity and recovery value of silicone oils are not available publicly. However, information for vegetable oils indicates that the overall problem of oily clays is substantial. Table XIV summarizes the characteristics of waste bleaching clays. On the basis of 12 billion pounds of vegetable oil produced annually, most of which is refined by bleaching, the waste clay volume is on the order of 86 million pounds per year. In a "typical" plant, the oil-laden clay rate is about 13,000 pounds per day.

Therefore, there appeared to be major incentives for testing the prospects for de-oiling spent clays using critical-fluid extraction.

TABLE XIV

CHARACTERISTICS OF WASTE BLEACHING CLAY

MAGNITUDE OF THE PROBLEM

VEGETABLE OIL PRODUCTION, U.S.: 12 BILLION LBS ANNUALLY

CLAY USE: 0.5 LBS/100 LB REFINED OIL

WASTE CLAY: ≅ 30% OIL

U.S. WASTE CLAY = 86 MILLION LBS/YR OF OILY CLAY = 330,000 LBS/DAY (5-day week)

"TYPICAL" PLANT

860 TONS IN 6 MONTHS

22-44% OIL

OILY CLAY RATE = 13,000 LBS/DAY

INCENTIVES FOR A NEW APPROACH

1. ELIMINATION OF THE HAZARD OF SPONTANEOUS COMBUSTION
2. REDUCTION OF HAULING COSTS
3. RECOVERY OF OIL PRODUCT
4. RECOVERY OF CLAY FOR REUSE

B. Test Apparatus, Procedures and Materials

1. Apparatus and Procedures

The experimental apparatus was similar to that used in the kilogram-scale mill scale runs. A sketch is given in Figure 7 (Section III). A fixed bed extraction column was used in all the experiments with bleaching clay, both silicone and vegetable oil. The extraction column was 152 cm long and 3.18 cm I.D. The column had two equally-spaced solvent inlet ports along the length of the extractor (i.e., at 1/3 and 2/3 the length of the bed). These ports were used when initially filling the vessel and when the extraction is first started. It was also equipped with ports at the bed entrance and exit.

A liquid flowmeter measured the cumulative solvent use. In line before the flowmeter was a sight glass to insure that liquid only was entering the flowmeter, to assure accurate solvent flow measurement. A piston pump metered the solvent into the system and boosted the system pressure. Pressure gauges at the inlet and discharge of the extractor measured the extraction pressure and pressure drop across the extractor. Thermocouples were used to monitor the extraction temperature. The extracted oil and solvent were collected in a Strahman sight glass. The solvent was vaporized and taken off the top; the oil was collected from the bottom.

In carrying out an extraction test, the column was filled with a known amount of bleaching clay. The ends were plugged with a filter cloth to prevent solids carry-over into the lines and valves.

The solvent initially was introduced to the bed at three points: the main inlet valve and the two valves along the side of the column. After the pressure in the column reached the solvent vapor pressure, the pump was used to increase the solvent flow and pressure within the system. When the desired pressure was reached, the flowmeter was reset and the metering valve to the oil/solvent collector was opened. The pump rate and the flow through the valve was equalized so that the flow was steady. When the collected oil had built up in the collector, it was drawn off into a sample jar and weighed (the amount of solvent was recorded simultaneously). At regular time intervals, inlet and outlet pressure, temperature, and solvent flow were recorded. After the flow rate was steadied, pressure drop across the bed was measured. The system was shut down when no further oil extraction was noted. After venting, the extractor was opened and the bed length remeasured. Then the bleaching clay was emptied from the column.

2. Bleaching Clay Samples

Available information concerning composition of bleaching clay samples is summarized in Table XV. Based largely on EPA's interest in specialty oils such as silicones, most samples were obtained from processing this product (three manufacturers). Four samples were drawn from one plant, covering a range of solids as well as two different oil viscosities.

A single soybean-oil clay sample was tested. The oil content was low; other refiners have indicated that oil levels of 30-50% in spent clay are more common.

3. Solvents

Three solvents were tested: propane, Solvent-12, and Solvent-500. Most testing was done with Solvent-500. This is an azeotropic mixture of 73.8 wt% dichlorodifluoromethane (solvent-12) and 26.2 wt% 1,1-difluoroethane. The use of this solvent was recommended by EPA during the program because it has a lower chlorine content (21). Lower chlorine is of interest because among the halogens chlorine has been implicated in ozone-layer degradation in the upper atmosphere.

C. Experimental Results

A summary of experimental extraction runs is given in Table XVI. Extraction curves are presented in Figures 13, 14, and 15.

1. Comparison of Solvents

Three runs were carried out in the 152-cm column to determine the effect of different solvents on extractions of oil from spent bleaching clay. A silicone oil clay was chosen because most samples were of this type. The vegetable oil clay sample was not tested with more than one solvent. Results are shown as extraction curves in Figure 13.

The comparison shows that propane is the superior solvent, reaching high levels of extractions with the lowest solvent use. Solvent-500 was next in effectiveness, followed by Solvent-12. The latter two were both reasonably effective, and close in performance.

Because of potential constraints on the use of propane due to costs of flammability protection, it was decided that testing of other clays should be done with Solvent-500.

TABLE XV

BLEACHING CLAY SAMPLES

SAMPLE CODE	SOURCE	OIL	SOLID	OIL CONTENT WEIGHT PERCENT
BC - S - 1a	1	Silicone	Unspecified Catalyst	54
BC - S - 1b	1	Silicone (low viscosity)	Celite and Na HCO_3	57
BC - S - 1c	1	Silicone	Celite and Na HCO_3	67
BC - S - 1d	1	Silicone	Acid Clay	52
BC - S - 2	2	Silicone	Unspecified	43
BC - S - 3	3	Silicone	Unspecified	63
BC - V - 1	4	Vegetable (Soybean)	Unspecified	17

TABLE XVI

SUMMARY OF BLEACHING CLAY EXTRACTION RESULTS

FEED MATERIAL	BC-S-1b	BC-S-1b	BC-S-1b	BC-S-1a	BC-S-1c	BC-S-1d	BC-S-2	BC-S-3	BC-V-1
OIL	SILICONE	SILICONE	SILICONE	SILICONE	SILICONE	SILICONE	SILICONE	SILICONE	VEGETABLE
SOLVENT	PROPANE	SOLVENT-12	SOLVENT-500	SOLVENT-500	SOLVENT-500	SOLVENT-500	SOLVENT-500	SOLVENT-500	SOLVENT-500
TEMPERATURE (^{o}C)	25	25	24	27	25	19-25	24	23	22
PRESSURE (atm)	9.2-20.7	14.6-21.4	14.6-18.0	14.6-61.2	14.6-19.4	14.6-42.2	12.9-20.7	13.3-16.0	13.9-30.3
PRESSURE DROP (atm)	2.4-9.2	0.7-4.8	0-1.4	5.1-48.3	1.4-4.4	6.1-34.0	1.0-4.8	0-3.7	2.4-20.4
SUPERFICIAL SOLVENT VELOCITY (cm/sec)	0.04-0.18	0.04-0.14	0.06-0.23	0.05-0.14	0.10-0.28	0.03-0.13	0.15-0.21	0.13	0.19-0.25
Feed Mass (g)	1000	970	1000	1000	1300	1150	740	1300	500
Residue Mass (g)	470	420	490	-	670	640	450	440	410
Oil in Feed (Soxhlet analysis) (g)	570	550	570	540	870	600	320	820	90
Oil Collected (g)	510	420	500	150	550	430	270	820	90
Oil in Residue (Soxhlet analysis) (g)	20	30	40	220	130	40	70	4	20
Collection Efficiency[1] (%)	89	76	88	28	63	72	89	100	100
Solvent Used (kg)	2.9	8.6	13.4	10.1	9.7	12.1	11.5	11.4	18.9
Solvent:Feed (mass basis)	2.9	8.9	13.4	10.0	7.5	10.5	15.5	8.8	37.8
Removal Efficiency[2]	96	95	93	59	85	90	78	99.5	78
Bed Compression (%)	39	-	0	-	0	-	14	0	14
Initial Bulk Density (g/cc)	0.84	0.80	0.86	0.80	1.08	0.97	0.62	1.07	0.42
Final Bulk Density (g/cc)	0.65	0.36	0.41	-	0.56	0	0.45	0.38	0.40

[1] Based on [(Oil Collected) ÷ (Oil in Feed)]

[2] Based on [(Oil in Feed-Oil in Residue)/Oil in Feed]

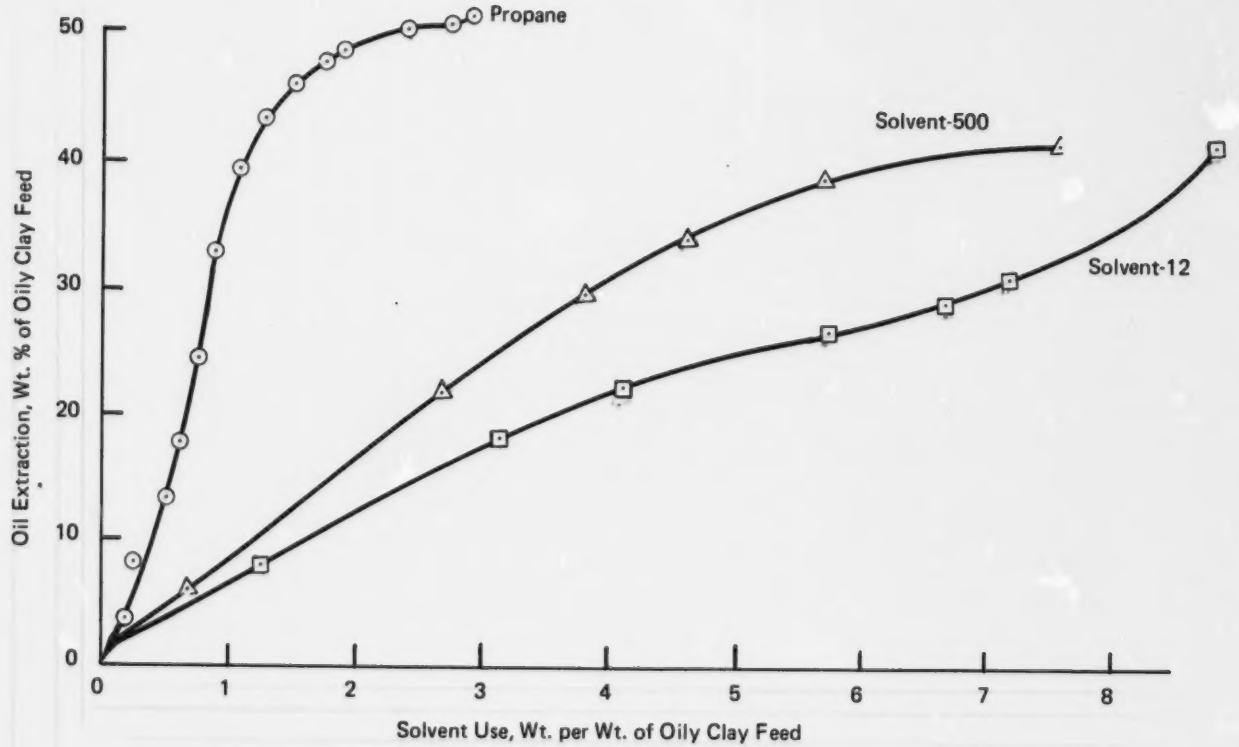


FIGURE 13 COMPARISON OF SOLVENTS SILICONE-OIL CLAY (SPL #BC-S-1b)

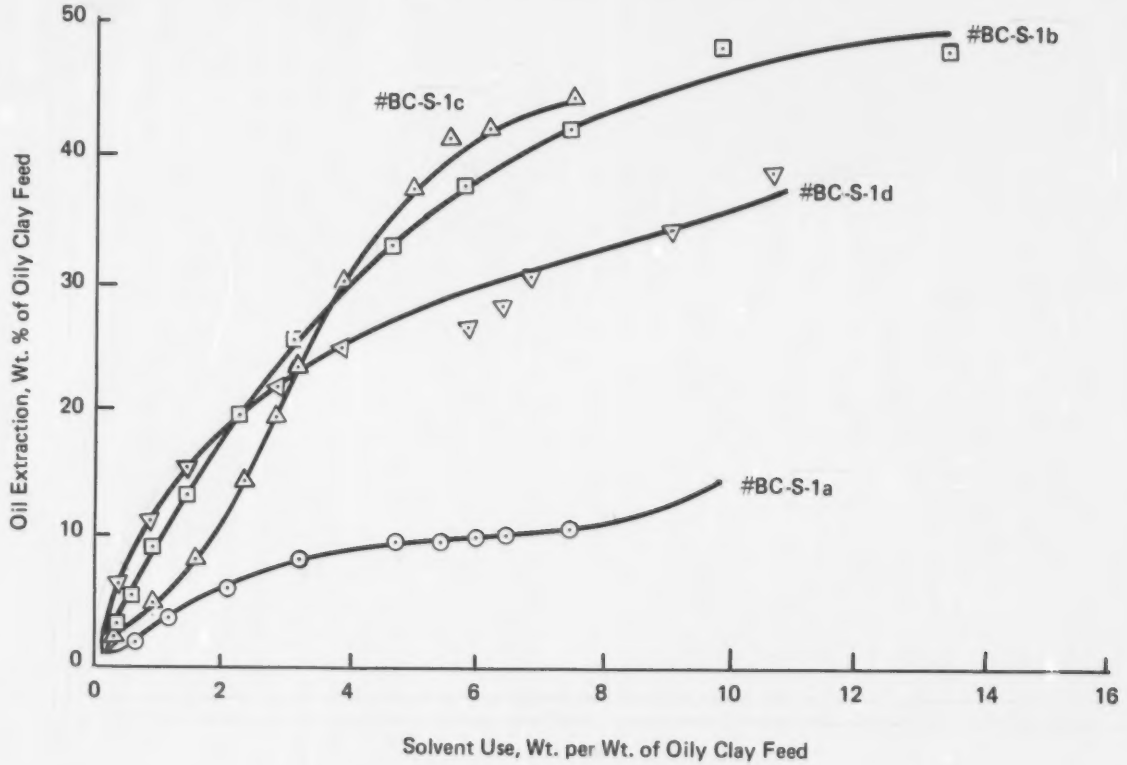


FIGURE 14 EXTRACTION CURVES SILICONE-OIL CLAYS WITH SOLVENT-500

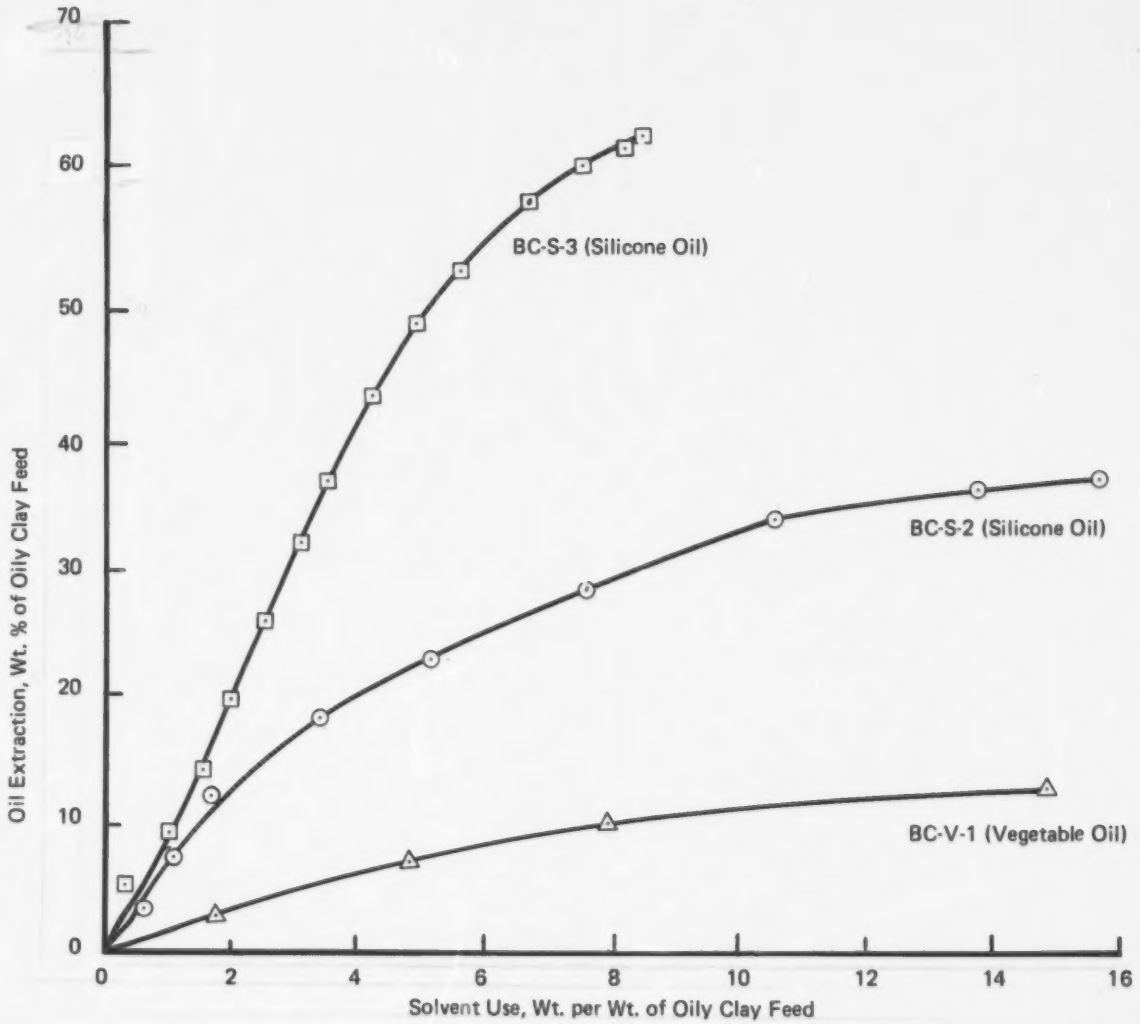


FIGURE 15 EXTRACTION CURVES SILICONE AND VEGETABLE OIL CLAYS SOLVENT-500

The extraction curve for Solvent-12 appears unusual in that its slope first decreases with increasing solvent use, and then increases. The initial decrease in slope is characteristic of the other extraction curves; the front of oil concentration passing down the bed during extraction is not a perfect step wave. Mass transfer resistance, minor flow non-uniformities over the bed cross-section, and the presence of some fraction of oil that is difficult for the solvent to access all may be contributing factors. The increasing slope, however, was probably due to a deliberate re-distribution of flow: because of erratic pressure drop problems in these beds, some flow of solvent was introduced in parallel into the downstream portion of the bed via the flow manifold (Figure 7). In the latter stages of the Solvent-12 extraction run, the manifold was closed and all flow was from the bed inlet. Apparently, some oil had remained in the upstream portion of the bed, and this was extracted with the surge of flow at the bed inlet, giving rise to the increased slope in the extraction curve. If this is so, then the terminal points of the extraction curves for Solvent-12 and Solvent-500 should be compared, and they are nearly equivalent. Thus, those two solvents may be equally effective for the silicone oil extraction.

2. Comparison of Feeds

Figures 14 and 15 give extraction curves using Solvent-500 for seven different spent bleaching-clay feeds.

It should be noted that all clays did not have the same oil level; thus the final extraction levels among these curves cannot be compared. However, the initial slopes would be the same if each bed had the same equilibrium characteristics, mass-transfer kinetics, and the same length. Indeed, samples BC-S-1b and -1c are similar (Figure 14), and samples BC-S-2 and S-3 are in the same range, also, in initial slope. The fact that 1b contains an oil with a lower viscosity probably indicates that the bed solids, rather than the oil, control the extraction characteristics among the silicone-oil clays. Samples 1b and 1c contained the same solids, and initial extraction slopes were similar.

The vegetable-oil clay sample exhibited a lower final extraction level because of lower oil content. However, it also showed a lower slope. There is insufficient information to distinguish the effects of oil composition (fatty-acid triglycerides in vegetable oil compared to silicone oils) or the nature of the solids.

In general, while acceptably high oil removals were achieved in most cases, these levels were not 100%. Sample 1a was the poorest, where only 26% of the initial oil was extracted.

With sample 1d, 37% was achieved, versus 52% in the feed. For sample 1c, 43% was achieved versus 67% in the feed. Better results were obtained with sample 2 (37% vs. 45% in the feed), sample 1b (49% vs. 57% in the feed), and sample 3 (63% vs. 63% in the feed). The vegetable oil sample V-1 had 13% extracted, compared to a 17% feed content.

At least some of these results are complicated by flow difficulties that occurred with most of the samples. During these tests there were periodic episodes of partial plugging of the bed, causing pressure and flow surges. Partial diversion of flow via the bed manifold connections was helpful in correcting the problem, but this produced inconsistencies in the flow pattern in the course of a single extraction run. Thus, the extraction curves cannot be interpreted quantitatively to any great degree. Most important, however, was the ultimate successful experience in handling flow through these fine particulate beds, to aide in future pilot plant studies.

3. Extracted Oil Quality

One silicone-oil manufacturer carried out a series of functional tests on a sample of extracted oil (S-3). The manufacturer stated that the extracted oil was acceptable as product according to standard specifications. The following specifications were not characterized quantitatively, but were indicated as acceptable compared to the corresponding silicone-oil product sold commercially: viscosity; flash point; acid value; and odor. Total chloride was 9 ppm, versus a specification of <20 ppm; weight loss (24 hours at 150°C) was 0.15% versus a specification of <0.5%. The latter two measurements indicated that there was adequate removal of residual solvent.

D. Process Economics

Preliminary process economics have been calculated for a plant capacity of 300,000 lbs/year, using sample BC-S-3 as a basis. This material contained 63% silicone oil, and it was assumed that a commercial extractor would perform as shown in the extraction curve in Figure 15. These criteria are summarized in Table XVII.

Cost figures are summarized in Table XVIII. The plant cost was estimated to be about $170,000 installed, as detailed in Table XIX. Annual operating costs, including depreciation and disposal of stripped solids, total $80,000. Based on information from industrial sources, the recovered oil, meeting product specification, may be valued at about $1.00 per pound. Thus, assuming 90% recovery of the feed oil (laboratory results were 100% for this sample), process credits should include about $170,000 for oil credits, plus savings in incineration costs for current disposal.

TABLE XVII

BLEACHING CLAY DE-OILING PLANT
(Silicone Oil)

DESIGN CRITERIA

CAPACITY:	300,000 lbs/yr. (136,000 kg/yr)
OPERATING FACTOR:	2,000 hrs/yr. (5 da/wk, 1 shift/day)
FEED OIL CONTENT:	63 wt%
SOLVENT:	Solvent-12 or -500
SOLVENT:FEED RATIO:	9.0
EXTRACTION TIME PER BATCH:	2 hours

TABLE XVIII

BLEACHING CLAY DE-OILING PLANT
(Silicone Oil)

OPERATING COSTS

ITEM	ANNUAL COST
Labor, 1 operator, $20/hr salary, fringes and overhead	$ 40,000
Electric power, 50 HP (37 kw) @ $0.075/kwh	5,600
Make-Up Solvent, 0.7 lbs/hr @ $0.70/lb.	1,000
Maintenance, @ 4% of $170,000 Capital Investment	6,800
Taxes, @ 2% of Capital Investment	3,400
Depreciation, @ 10% of Capital Investment	17,000
Solids Disposal, @ $0.05/lb.	6,500
TOTAL ANNUAL COST	$ 80,300

Cost Per Pound of Spent Clay: $0.27

Cost Per Pound of Recovered Oil (90% yield): $0.47

TABLE XIX

BLEACHING CLAY DE-OILING PLANT

CAPITAL COST

Equipment:		
Extractor	$16,000	
Compressors	12,000	
Stripper	6,000	
Heat Exchanger	5,000	
Tanks, Pumps	18,000	
Skid	8,000	
Instruments	20,000	
		$ 85,000
Engineering, Assembly, Installation		60,000
Contingency		25,000
		$170,000

VII. WASTE OIL-WATER EMULSIONS

A. Nature of the Problem

Waste oil-water emulsions from industrial processes may be derived from a wide range of sources. Common among these are waste lubricating emulsions in the metal machining and forming industries. For these laboratory studies, two types of wastes were selected for testing critical-fluid solvent extraction for oil removal. One was from aluminum can-forming operations, and the other from various steel mill operations. In the first case, a composite waste was obtained from a single manufacturer. In the other case, two manufacturers' samples were tested.

Aluminum cans are made primarily for the beverage industry. Manufacturers are both the beverage producers and aluminum companies. In forming the product, an emulsion is used in the various metal-working operations. One concentrate formulation is given in Table XX; the concentrate is diluted ten-fold with deionized water, and in some cases is spiked with a petroleum-based oil. Most of the lubricant formulation is recycled, but a bleed stream (tramp oil) containing contaminating solid fines is taken off and hauled away at costs in the range of $0.15-0.25 per gallon. Even partial removal of the oil would be beneficial: oil recovery for fuel value (about $0.60 per gallon of oil) or recycle lubricant (about $5 per gallon of oil) would provide an offset against processing costs. Reduction in oil content may permit less expensive treatment of the wastewater.

Specific aluminum can-forming operations contributing waste emulsions include the following:

a) Cupping presses, where cans are drawn and formed from a brick;

b) Briquetting, where off-quality cans are recycled;

c) Recycle-lubricant centrifuge, which processes spent lubricant to spin off tramp oil;

d) Soluble-oil hold tank, into which the total system is dumped from time to time when bacteria buildup becomes intolerable;

e) Drum and rope skimmer hold tank, containing skimmings from can washing and etching processes.

TABLE XX

COMPOSITION OF LUBRICANT CONCENTRATE FOR ALUMINUM CAN FORMING

COMPONENT	WEIGHT PERCENT
Ethoxylated/Propoxylated Alcohols	28
Unsaturated Diols	4
Fatty Acids	6
Triethanolamine	6
Amine Borate	2
Benzylic Acid Derivative	1
Water	53

Supplier: S.H. Mack & Co., St. Charles, IL

One analysis of a waste oil emulsion from these operations is the following:

Free Oil	13.2%
Dissolved Hydrocarbons (oil)	3.87%
Suspended Solids	0.08%
Water (est.)	83%

As shown below from laboratory samples, this oil content appears to be high; oil contents for such wastes were measured to be in the range of 1-5%.

The second type of waste oil emulsion tested was from steel-mill lubricants. Details of sources and quantities of lubricating-oil wastes in steel-product forming were presented in Section III. Two liquid wastes were obtained from steel-mill "basins" which carry out a rough separation of oil, water, and solids from the combined wastes resulting from many mill operations.

The combined wastes flow at a low velocity along the length of the basin, which serves as a sedimentation tank. Solids, with entrained oil and water, settle to the bottom, from which they are removed on a continuous moving-belt grate. Oil rises to the surface and is skimmed, often with a rope skimmer which sponges up oil floating on the surface. The water is pumped to sand-bed filters, and in some cases adsorption columns. A sludge is backflushed from the sand beds and combined with the sedimented solids.

The samples tested here were liquid waste drawn together with sediment. As in the case of aluminum-can emulsion wastes, oil recovery should be possible, and would provide the benefits of oil recovery for fuel and reduced downstream treatment costs for the residual water.

B. Experimental Apparatus and Procedures

A diagram of the experimental apparatus is shown in Figure 16.

A Strahman sight glass with a volume of 820 ml was used as the extraction vessel for the emulsions tests. It was equipped with a stirrer and a cooling water coil. A piston pump was used to move the solvent through the emulsion. U-tubes were the separation/collection device for the oil and solvent. A Dry Test Meter (DTM) was used to measure the flow of solvent.

To carry out the extraction test, the sight glass was charged with the emulsion feed. Solvent was added and the pressure increased to the desired level. Once the operating pressure was reached, the mixture was stirred for maximum solvent and feed contact. The sample valves were then opened to the U-tube collector and DTM. At specified time intervals the U-tube was changed and the temperature, pressure and solvent use were noted. The U-tubes were changed until no additional oil extract appeared. When the extraction was complete, the solvent cylinders were closed and the pump shut off. The sight glass was depressurized through the U-tube and DTM. After the depressurization, the residue was collected and weighed.

Feeds and extraction residues were analyzed by determining weight loss, after evaporation to dryness, to give moisture and volatiles content. The dry residue was analyzed for oil and solids by thermal gravimetric analysis (TGA), assuming solids were non-combustible inorganics.

Solvents used were carbon dioxide, propane, halocarbon Solvent-12, and halocarbon Solvent-500. These have been described in Sections III and IV.

C. Experimental Results

A summary of experimental tests carried out with waste oil emulsions is given in Table XXI.

The aluminum can forming emulsion was a mixture of water, aluminum fines and oil. It was a homogeneous mixture with a grey color, not opaque. If allowed to settle, small black oil droplets floated to the surface. When thoroughly mixed, a representative sample could be taken. Such samples were analyzed by TGA.

Steel mill emulsion-I was the liquid decanted from a mill-scale sample. It contained largely water plus lubricating oil and metal fines. The moisture and volatiles content could be measured by evaporation to dryness, thus also giving a solids-plus-oil content. The oil content alone could not be measured with any precision because the sample contained a non-uniform distribution of oil on the surface. The water content of various samples could not be replicated well either. Thus, oil contents shown were back calculated from amounts extracted.

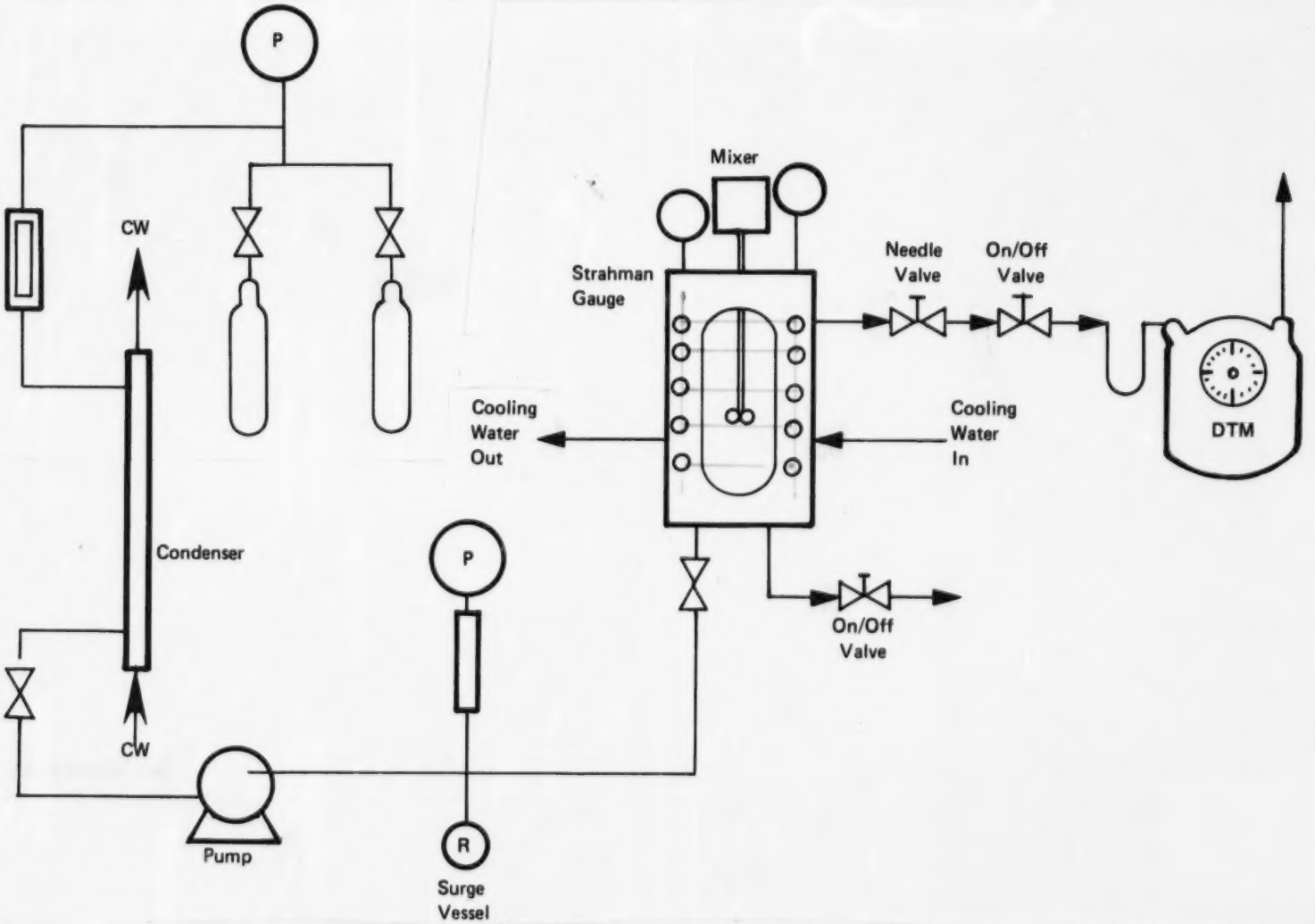


FIGURE 16: EXPERIMENTAL SYSTEM FOR EMULSIONS EXTRACTION TESTS

TABLE XXI

SUMMARY OF EXTRACTION RUNS WITH WASTE-OIL EMULSIONS

SAMPLE NO.[1]	1	4	5	6	8	2	3
FEED	Aluminum Can-Forming Emulsion	Aluminum Can-Forming Emulsion	Aluminum Can-Forming Emulsion	Aluminum Can-Forming Emulsion	Aluminum Can Forming Emulsion	Steel-Mill Emulsion-I	Steel-Mill Emulsion-II
SOLVENT	SOLVENT-500	SOLVENT-12	CARBON DIOXIDE	PROPANE	CARBON DIOXIDE	SOLVENT-500	SOLVENT-500
TEMPERATURE (°C)	26	26	29	24	23	27	29
PRESSURE RANGE (atm)	11-64	15-55	62-69	15-19	66-86	18-28	15-24
FEED WEIGHT (g)	438.6	416.7	390.2	296.1	399.45	457.9	419.6
TOTAL SOLVENT USED (g)	2762	5390	3345	375.8	3335	3390	2879
TOTAL OIL COLLECTED (g)	1.2	0.51	1.61	.53	3.63	0.92	0.13
RESIDUE (g)	421.8	417.7	354.9	276.2	352.25	428.8	399
TOTAL OIL COLLECTED (% of Feed)	0.27	0.12	0.41	0.18	3.63	0.20	0.03
OIL IN FEED[2] (g)	7.02	6.67	6.24	4.74	6.39	0.21	0.08
OIL IN RESIDUE[2] (g)	5.91	5.64	2.56	3.42	2.25	-	-
COLLECTION EFFICIENCY[3] (%)	17	8	26	11	57	-	-
REMOVAL EFFICIENCY[4] (%)	16	15	59	28	65	-	-

[1] See Table XXII

[2] Based on Data in Table XXII

[3] Based on [(Oil Collect/Oil in Feed)]

[4] Based on [(Oil in Feed-Oil in Residue)/Oil in Feed]

Steel mill emulsion-II was also decanted from a mill scale sample. Again, it is made up mostly of water with a random surface oil distribution of oil. A representative sample could not be taken due to non-uniformity.

Each sample was extracted with at least one of the following solvents: carbon dioxide, propane, Solvent-12, or Solvent-500. The results of the feed and residue analyses are summarized in Table XXII. It is evident that there are significant discrepancies between the collection efficiency, based on the collected oil figure, and the removal efficiency calculated from feed oil level minus residue oil level. The collection efficiency figures are more reliable, as described in Appendix A.

In the extractions with the halocarbon solvents and with propane, major difficulties were experienced with formation of complex emulsions. The mixtures at high-pressure process conditions were visible in the sight gauge, and it was apparent that adequate phase separation between solvent and feed did not occur consistently. Thus, during the test, there was intermittent carry-over of feed with the solvent stream.

With CO_2, this was not a significant problem, and effective phase separation occurred with the exception of some feed carry-over in the initial extract samples. The more favorable phase behavior of CO_2 must be considered an important factor in solvent selection.

Fortunately, CO_2 also has favorable solvent capability relative to propane and the halocarbons. Other experience has shown that CO_2 generally has less solvent capability for hydrocarbon oils than halocarbon and hydrocarbon solvents. However, as shown in Table XXII, much of the oil used as lubricant in aluminum can forming represents oxygenated organics such as ethoxylated and propoxylated alcohols, and CO_2 is a relatively good solvent for these liquids (9).

An approximate figure for the degree of extractions, or oil yield, can be obtained from the ratio of extracted oil to feed oil. For the CO_2 test, this figure is 57%, which is quite favorable for a single-stage extraction. Higher yields can be obtained simply by using a multiple stage counter-current liquid-liquid extraction column. Such columns have been operated with high-pressure liquid or supercritical CO_2 for homogeneous solutions as well as for feed liquids containing suspended solids (20).

TABLE XXII

FEED AND RESIDUE ANALYSIS

SAMPLE	FEED ANALYSIS							RESIDUE			
	NO. OF SAMPLES	OIL & SOLIDS wt %	OIL[2] wt %	SOLIDS[2] wt %	FEED WEIGHT	OIL EXT. (g)	% of FEED	NO. OF SAMPLES	H_2O[1]	OIL[2]	SOLIDS
1 Aluminum Can-Forming Emulsion, Solvent-500	3	2.0	1.6	0.4	438.6	1.2	0.27	1	98.19	1.40	0.40
2 Steel-Mill Emulsion-I, Solvent-500	1	1.17	---	---	457.9	0.92	0.20	1	99.83	0.50	0.12
3 Steel-Mill Emulsion-II, Solvent-500	1	0.32	---	---	419.6	0.13	0.03	1	99.93	0.02	0.05
4 Aluminum Can-Forming Emulsion, Solvent-12	3	2.0	1.6	0.4	416.7	0.51	0.12	1	98.35	1.35	0.30
5 Aluminum Can-Forming Emulsion, CO_2	3	2.0	1.6	0.4	390.2	1.61	0.41	1	99.03	0.72	0.25
6 Aluminum Can-Forming Emulsion, Propane	3	2.0	1.6	0.4	296.1	0.53	0.18	1	98.52	1.24	0.24
7 Aluminum Can-Forming Emulsion, CO_2	3	2.0	1.6	0.4	399.45	3.63	0.91	1	99.13	0.64	0.23

[1]Based on oven drying to remove water

[2]Based on TGA Analysis

A comparison of this solids contents of the residue samples from the aluminum can forming waste indicated a variable degree of solids reduction. The solvent-500 residue, for example, showed no change in solids (0.4% vs. 0.4%). In contrast, the propane extracted sample showed a reduction from 0.4% in the feed to 0.24% in the residue. It is probable, however, because of sample variability, that there is no significant difference, and the reductions in solids contents due to extraction may be negligible.

The steel mill emulsions were tested with solvent-500 only. The results are difficult to interpret because of feed-solvent-emulsion formation, and because the feed samples gave no consistent TGA values for the oil vs. solids content. Thus, without feed oil contents, neither extraction nor collection efficiencies were calculable. It can only be noted that some oil extraction was obtained.

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APPENDIX A

QUALITY CONTROL EVALUATION REPORT

I. Summary

A.1) Purpose of Project

The purpose of the project is to evaluate the feasibility of using critical fluids to extract oil from industrial waste samples, and to provide the preliminary engineering data necessary for the design and operation of a pilot plant. The waste streams selected for this study were:

a) Oil-laden bleaching clays from specialty oil and vegetable oil decolorization and clarification.

b) Oily mill scale from the steel industry.

c) Lubricating oil-water waste emulsions from the aluminum and steel industry.

A.2) Purpose of Q.C.E.R.

The Quality Control Evaluation Report (Q.C.E.R.) is a report on the data quality and the research results in terms of precision, accuracy, completeness, and comparability, as well as a semi-quantitative assessment of the results and conclusions.

B. OVERALL EVALUATION:

A Quality Assurance Project Plan was not submitted prior to this project, and as a result no formal Quality Control Program was in effect during the course of these experiments. However, in the 3 major areas of data generation in our laboratories (App. A, Sec. II), material balance calculations and calibration procedures were used as a standard practice to evaluate the accuracy of results. A summary of the procedures used to determine the reliability of data for bleaching clay and mill scale samples is presented in Table A1. Also in Table A1 is the maximun error in accuracy of any of the individual measurements reported which show that the extraction data for bleaching clay may be 53% lower, or 34% higher than the actual value. From mill scale extraction, it can only be said that the maximum error in accuracy may be even higher due to the small quantities of oil collected.

Table A7 shows that the accuracy of the soxhlet technique used to determine feed and residue oil contents is within 7.5% (0.78 mass %) of the true value, although a larger problem may exist in the sampling methods used to obtain representative aliquots of both.

As noted in the main text (sec. VII), the analytical laboratory results pertaining to emulsion samples were inconsistent and difficult to interpret, resulting in qualitative assessments of the extraction capabilities of critical fluid solvents. The quality control evaluation for this phase of the project is treated separately in Appendix A, Section III.

TABLE A1

OVERALL ACCURACY OF DATA COLLECTED FOR BLEACHING CLAY AND MILL SCALE SAMPLES

DATA COLLECTED	UNITS OF MEASUREMENT	METHOD OF DETERMINATION	RELIABILITY TEST	MAXIMUM ACCURACY ERROR (%) Bleaching Clay	Mill Scale
Extract Oil Mass	$\frac{\text{Mass Oil (g)}}{\text{Time (min)}}$	Direct Flashing of Extract into Oil Collection Vessel	Material Balance Calculation	- 21.0% + 2.0%	-- + 2.0%
Solvent Flow Rate	$\frac{\text{Mass Solvent (g)}}{\text{Time (min)}}$	Solvent Flow Measurements Using Liquid Flowmeter	Manufacturers Spec. and Comparison With Calibrated Dry Test Meter	± 32.0%	±32.0%
Feed and Residue Oil Fraction	$\frac{\text{Mass Oil (g)}}{\text{Mass Sample (g)}}$	Conventional Soxhlet or Butt Tube Bench Scale Oil Extractions	Material Balance Calculations and a Subsequent Investigation Using Prepared Standards.	± 7.5%*	--

*Does not include errors of sampling.

II. DATA GENERATION AND METHODOLOGY

The results presented in this report are based upon three principle sets of experimental data:

a) The mass of oil extracted and collected during critical fluid extraction.

b) Critical fluid solvent flow rates.

c) Feed and residue oil content.

Of these three sets of generated data, the first two were used directly to generate critical fluid extraction curves for bleaching clay and mill scale waste samples (Fig. 8 thru 15), while the third was used primarily to determine the extent to which extraction had occurred.

a. Extract Sampling During Critical Fluid Extraction

To determine the fraction of oil in the extract stream, the extract was flashed (from about 15 atm pressure to 1 atm) across a needle valve and sent to a sight gauge used as an oil collection vessel. From there the solvent vapor was continuously removed through an exit port at the top, and the oil was collected and drained intermittently from the bottom (Fig. A1).

The mass (g) of oil drained from the sight gauge was recorded along with the corresponding flow of solvent into the extraction vessel (App. A, Sec. II, b) to determine the fraction of oil in the extract line (x_o) during a given time interval. This fraction is calculated as:

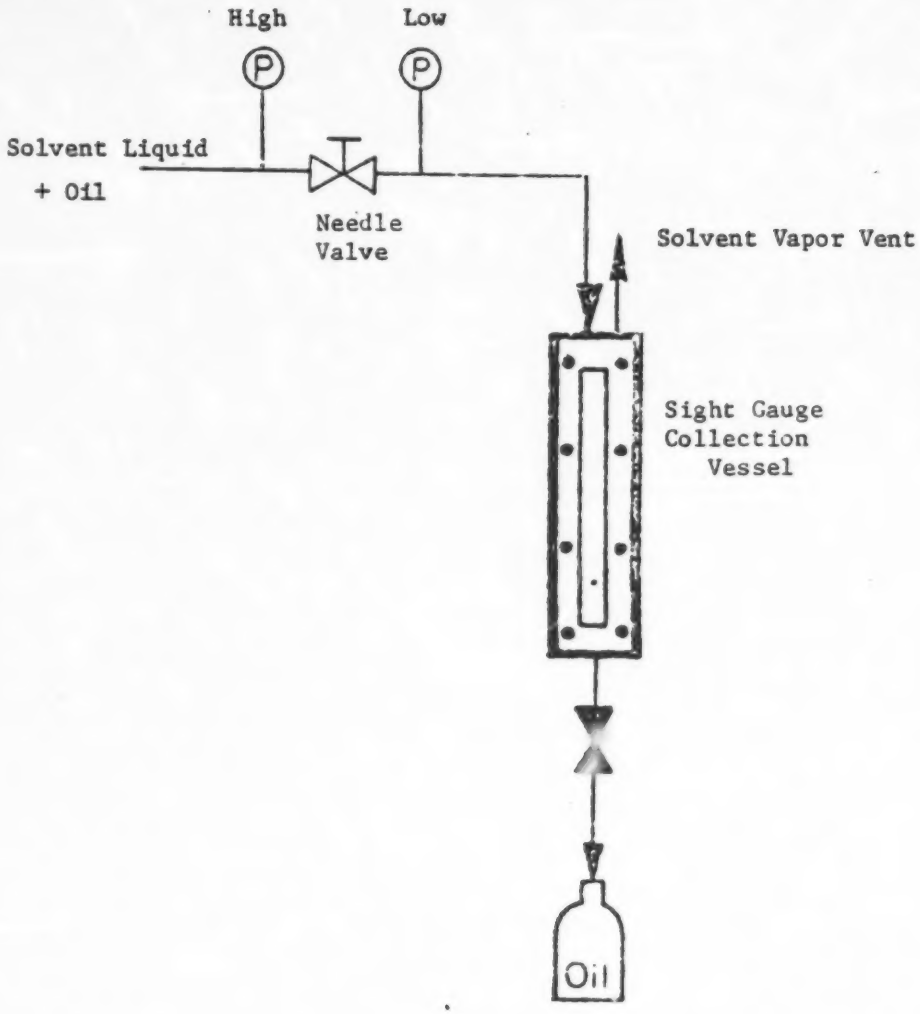
$$x_o = \frac{\text{Mass Oil (g)}}{\text{Mass Solvent (g)} + \text{Mass Oil (g)}} \qquad \text{(Eq. 1)}$$

In this oil collection procedure, the possible sources of error that could have affected the accuracy of the results are:

- Entrainment of oil in the vapor exit which would result in low readings.
- Dissolved gas (solvent) in the oil collected which would result in high readings.
- Errors in weighing.

FIGURE A1

OIL COLLECTION APPARATUS USED DURING BLEACHING CLAY AND KILOGRAM MILL SCALE CRITICAL-FLUID EXTRACTION



Oil Collection Jar

Entrainment of Oil in Vapor Exit

BLEACHING CLAYS

As a first step towards calculating the maximum value for this first source of error, Table A2 lists each bleaching clay extraction and its corresponding material balance closure, where material balance closure (M.B.C.) is defined as: (Eq. 2)

$$\% \text{ M.B.C.} = \frac{(\text{Mass Oil Collected (g)} + \text{Mass Residue (g)}) \times 100}{\text{Mass Feed (g)}}$$

Table A2 also shows the total mass loss for each extraction, where mass loss (M.L.) is defined as:

$$\text{M. L.(g)} = \text{Feed Mass (g)} - \text{Residue Mass (g)} - \text{Oil Mass (g)} \quad \text{(Eq. 3)}$$

A conservative assumption that all of the mass loss (Table A2) is due to oil lost through the vapor exit port leads to a calculation of the maximum error in accuracy associated with (a) vapor entrainment, where:

$$\frac{\text{Mass Loss (g)} \times 100}{\text{Mass Oil (g)} + \text{Mass Loss (g)}} = \text{Max. Error (\%) Due to vapor entrainment of oil.} \quad \text{(Eq.4)}$$

Results of this analysis are presented in Table A3.

TABLE A2

MATERIAL BALANCE CLOSURES FOR BLEACHING CLAY EXTRACTIONS*

EXPERIMENT NUMBER	FEED (g)	RESIDUE (g)	OIL (g)	MATERIAL BALANCE CLOSURE (%)	MASS LOSS (g)
2	1016.5	486.3	498.4	96.9	31.8
3	1283.0	666.4	547.7	94.6	68.9
4	1149.0	639.9	430.7	93.2	78.4
6	1002.0	466.0	513.4	97.7	22.6
7	944.7	706.5	188.5	94.7	49.7
8	735.5	453.6	273.7	98.9	8.2
17	1264.5	443.8	761.8	95.3	58.9

*Two extractions not included where incomplete material balance measurements were taken.

TABLE A3

MAXIMUM ERROR IN ACCURACY OF OIL COLLECTION METHOD DUE TO VAPOR ENTRAINMENT

EXPERIMENT NUMBER	MASS LOSS (g)	MASS OIL COLLECTED (g)	MAXIMUM ERROR DUE TO VAPOR ENTRAINMENT*
2	31.5	498.4	- 5.9%
3	69.3	547.7	- 11.2%
4	78.4	430.7	- 15.4%
6	23.0	513.4	- 4.3%
7	49.7	188.5	- 20.9%
8	8.1	273.7	- 3.4%
17	59.4	761.8	- 7.2%

*Error must be negative because oil collected can only be less than or equal to oil extracted.

Although the average value for the maximum error due to vapor entrainment is large (9.7%), the effect of this error is to decrease the reported value of the extract oil concentration (Fig. 13, 14, 15 - main text), making the critical fluid extraction process appear less efficient than it actually is.

MILL SCALE

The method of analysis used to evaluate the maximum error in the oil collection technique due to vapor entrainment for bleaching clays is inappropriate for mill scale samples due to the relatively small quantities of oil collected (Tables VI, VIII Main Text), but for purposes of estimation we may assume that they are approximately equal (max. error = 21%).

Maximum error in oil collection method due to dissolved gas (solvent) in oil.

Bleaching Clays and Mill Scale:

At atmospheric conditions, the mass of gas dissolved in the oil collected would be small compared to the mass of the oil, and can be shown to be less than 1% using Henry's Law which states that the mole fraction of dissolved gas in a liquid solution is proportional to the partial pressure of that gas (approx. 1 atm) divided by a constant (Eq. 5).

$$x_a = \frac{P_a}{H} \qquad \text{(Eq. 5)}$$

where: x_a = mole fraction dissolved gas.

P_a = partial pressure of dissolved gas

H = Henry's constant.

Unfortunately, Henry's constants are not readily available for propane and solvent-12, but for CO_2, $H = 1.25 \times 10^6$. (1)

$$x_a = \frac{760 \text{ mm Hg}}{1.25 \times 10^6} = 0.00061 = 0.061 \text{ mole \%}$$

(1) International Critical Tables, Vol. 3, p. 260, McGraw Hill Book Co., 1928.

Furthermore, if we consider that the molecular mass of the solvent is approximately 10% of the molecular mass of the oil, then the mass % of dissolved solvent in the oil collected is calculated to be 0.0061 mass %. A conservative estimate that the maximum concentration of dissolved solvent in oil is less than 1% allows for variations in the values of Henry's constants for propane and solvent-12 relative to CO_2.

The effect of this accuracy error (maximum of +1%) would be to increase the reported value for the extract oil concentration (Fig. 8-13 main text), making the critical fluid extraction process appear more efficient.

c. Errors in Weighing

Bleaching Clays and Mill Scale

The accuracy of the balance (top loading) used during these experiments has been tested and found to be readable to ±0.1 g. When this value (±0.1 g) is multiplied by the number of samples taken during an extraction (ave. = 5), and added to the number of feed and residue weighings taken, its cumulative effective on accuracy is less than or equal to 1%.

(b) Critical Fluid Solvent Flow Rate Measurements

Bleaching Clays and Mill Scale

For all bleaching clay and kilogram scale mill scale extractions, a liquid Bearingless* flowmeter recorded the flow of solvent into the extraction column, and at steady state this is a good approximation of the flow of solvent out of the column for a given time interval, (Ave: 10-20 min.). In addition, during six emulsion extractions, both the liquid flowmeter and a calibrated dry test meter** were used to record the flow of solvent into and out of the vessel, and a comparison of these two methods is presented in Table A4.

Table A4 shows that the difference between the liquid and vapor flow readings may be as high as 32% for some extractions due to either inaccurate readings by the meters themselves or non-steady state conditions within the extractor.

* Flow Systems Corp., 1420 Providence Highway, Norwood, MA
** American Meter Division, 13500 Philmont Avenue, Philadelphia, PA

TABLE A4

COMPARISON OF LIQUID (INPUT) VS. VAPOR (OUTPUT) SOLVENT FLOW MEASUREMENTS

EXPERIMENT NUMBER	LIQUID (IN) (g)	VAPOR (OUT) (g)	DIFFERENCE* (%)
10	2261.8	1538.3	32.0%
11	3390.4	3317.4	2.2%
12	2879.6	2203.1	23.5%
13	3139.4	2668.9	15.0%
14	3588.2	3218.9	10.3%
15	2349.0	3444.7	31.8%

$$*\text{Difference} = \left| 1 - \frac{\text{VAPOR (g)}}{\text{LIQUID (g)}} \right|$$

At the time of purchase (Nov., 1982), performance tests on the liquid flowmeter showed an accuracy to within ±1.0%, somewhat worse than the manufacturers stated accuracy of 0.05% (App. A, Sec. VI).

The manufacturer also publishes a warning that any vapor entering the flowmeter will lead to inaccurate readings but a sight glass permanently installed upstream of the meter gave us confidence that no vapor was present.

Two of the four dry test meters used in our lab were calibrated 10 days prior to the start of this project and showed a maximum error of ±2.5%, again somewhat higher than the manufacturer's stated accuracy of ±1.0%, (App. A., Sec. V).

Table A4 also shows that in five of six extractions, the liquid meter showed a higher reading (g) than did the vapor flowmeter, and this indicates that steady state conditions (Mass In = Mass Out) may not have existed in the extractor.

In order to achieve steady state for a multi component system, temperature, pressure, and composition must be held constant over a given time interval. As oil is removed from the feed, an equal volume of solvent must displace it in order to maintain a full liquid level in the extractor, in which case solvent in will not equal solvent out. This same conclusion holds for any carryover of feed during start-up, system leaks or spills of oil or solvent or a situation where the column is not completely full of liquid during extraction.

It is difficult to determine conclusively which of these possible sources of error resulted in the inconsistent readings of vapor vs. liquid solvent flow (Table A4), but in all of the extraction data presented in this report with the exception of the bench scale mill scale and emulsion runs, the liquid flowmeter readings were used, which generally showed the highest solvent use resulting in the lowest efficiency of extraction.

(c) Conventional Soxhlet[2] and Butt Tube Extractions to Determine Oil Content of Residue Samples

In general, the oil is extracted from a pre-dried solid sample using a liquid solvent (solvent 113, acetone, petroleum ether), after which the solvent is evaporated in a vacuum oven at 60°C. The oily residue is weighed (g), and its mass is divided by the mass of the initial solid sample to determine the weight fraction of oil. This method has been designated by the American Oil Chemists' Society as the most reliable (AOCS stated precision ±0.47 wt%), and the most commonly used for vegetable oil extraction.[3]

[2]USEPA, Manual of Methods for Chemical Analysis of Water and Wastes, p. 226, EPA - 625/6-74-003, 1974

[3]Meldenhahl Analysis of Fats and Oils, p. 15, The Gerard Press Publishers, Champaign, IL

Under a separate program performed subsequent to the time of the experiments presented here, a quality control program was initiated in our laboratories to determine the precision and accuracy of the soxhlet extraction technique on bleaching clays and results of this program are presented in Tables A5 and A6.

TABLE A5

ANALYSIS OF PREPARED STANDARDS TO DETERMINE ACCURACY

PREPARED OIL CONTENT OF STANDARDS (mass %)	OIL CONTENT BY SOXHLET EXTRACTION (mass %)	ERROR (mass %)	ERROR (%)
0 (clay + no oil)	0.26	0.26	---
0 (clay + no oil)	0.12	0.12	---
4.19	4.10	0.09	-2.1%
4.75	4.68	0.07	-1.5%
10.86	10.08	0.78	-7.2%
10.55	10.06	0.49	-4.6%
18.61	17.89	0.72	-3.9%
21.60	20.95	0.65	-3.0%

TABLE A6

ANALYSIS OF CONTROL SAMPLES TO DETERMINE PRECISION

DATE	SOXHLET RESULTS (mass %)	DEVIATION FROM MEAN* (mass %)
9-04-84	19.53	0.77%
9-10-84	20.84	0.54%
9-16-84	20.10	0.20%
9-16-84	20.30	0.0 %
9-20-84	20.75	0.45%

*Mean Value = 20.30 mass %

Details of the procedure used to prepare standards and controls are presented in Appendix A, Section VI.

If we exclude the blank samples, Table A5 shows that the value obtained by soxhlet extraction is always lower than the actual value (ave. error = -0.47%), which may be due to irreversible adsorption of oil by the bleaching clay. Conversely, the background value obtained for the blanks is always positive (mean = 0.19 mass %), and is due primarily to extraction of the sample holder (cellulose) and solvent residue after evaporation.

A statistical analysis of the data presented in Table A6 results in a standard deviation of 0.531, and a 0.95 probability that the values are within 1.07 mass % of the mean.

Although this analysis shows that the soxhlet technique itself is reliable, a larger problem exists in the sampling methods used for the feed and residue samples. Bleaching clay samples were sent to us in 5 gallon pails, and in some cases the solids had settled to the bottom leaving several inches of oil floating at the top. A slurry was made based on the volumetric proportion of each phase, and this was used as feed for critical fluid extraction and soxhlet analysis. Error may be introduced using this sampling method by assuming a constant concentration of oil throughout the solid phase, and this error is carried proportionately into soxhlet feed values for oil content. A material balance analysis of feed oil concentrations determined by soxhlet analysis is presented in Table A7.

If we assume an error in the oil collection technique of less than 10% (App. A, Sec. IIa), and that the sampling method used for residues is representative, then the discrepancy between the residue oil concentrations by soxhlet analysis and material balance calculations may be primarily due to inaccurate methods of feed sampling, and in the worst case (Exp. #4), may result in errors of 30 mass % oil.

In general, feed sampling for both bleaching clays and mill scale samples was a difficult problem to overcome, although at the present time greater care is taken to mix samples completely in order to obtain more representative samples.

TABLE A7

COMPARISON OF RESIDUE OIL CONCENTRATIONS
(MATERIAL BALANCE VS. SOXHLET EXTRACTION)
FOR BLEACHING CLAY EXTRACTIONS

Exp. #	Feed Mass (g)	Oil in Feed (Soxhlet) (g)	Oil Collected (g)	Residue Oil Concentration (Soxhlet) (%)	Residue Oil Concentration (Material Balance) (%)
1	1006	333	148	14.5%	21.6%
3	1283	639	548	5.0%	12.5%
4	1149	624	431	1.0%	26.9%
5	966	447	417	7.4%	5.5%
9	496	90	91	2.5%	0.0%

III. WASTE OIL-WATER EMULSIONS

As noted in the main text (Sec. VII), extraction results for emulsions (Table XXII) were difficult to interpret because of feed-solvent emulsion formation, and because feed samples gave no consistent TGA* values for the oil vs. solids content. Thus, without feed oil contents, neither extraction nor collection efficiencies were calculable. It can only be noted that some oil extraction was obtained.

*DuPont Model 950 Thermogravimetric Analyzer records weight changes as a sample is program heated for a specified time - max. temp = 1200°C. Tests performed at Analytical Chemistry Laboratories, Arthur D. Little, Inc.

IV. APPLICATION TO DESIGN

The Q.C. data evaluation presented here for bleaching clay and mill scale extractions (App. A, Sec. II) indicate that errors in our oil collection method and solvent flow measurements tend to decrease the reported effectiveness of critical fluid extraction rather than enhance it. However, due to the unknown error involved in feed and residue sampling for soxhlet analysis, a worse case scenario has been prepared, in which it was assumed that the true oil extract concentration is 50% lower than the reported experimental value, and that exactly twice as much solvent would be necessary to complete the de-oiling process. The corresponding changes in design criteria, capital and operating costs were then compared to the base case presented in the main report (Sec. VI) for a 300,000 lb/yr bleaching clay de-oiling plant.

For simplicity, the six-tenths factor rule was used to scale up new equipment costs, which states that:

$$\text{Cost of Equipment A} = \text{Cost of Equipment B}\left[\frac{\text{(Capacity of Equipment A)}}{\text{(Capacity of Equipment B)}}\right]^{0.6}$$

The result of this comparison, presented in Tables A8 and A9, show that being off by as much as a factor of 2 only increases the capital cost by 35% and the operating cost by about 20%. Since results were far more accurate, the impact on the estimates is certainly within the accuracy of the estimates themselves.

TABLE A8

THE EFFECT OF DOUBLING THE SOLVENT-TO-FEED RATIO ON THE CAPITAL COST OF A 300,000 lb/yr BLEACHING CLAY DE-OILING PLANT

Equipment	Base Case ($)	2 x (S/F) Ratio ($)
Extractor	16,000	20,000*
Compressors	12,000	19,000
Stripper	6,000	9,000
Heat Exchanger	5,000	8,000
Tanks, Pumps	18,000	27,000
Skid	8,000	12,000
Instruments	20,000	20,000
Sub Total	85,000	115,000
Engineering & Installation	60,000	80,000
Contingency	25,000	35,000
TOTAL	170,000	230,000

*Based on Bleaching Clay void Volume of 50%.

TABLE A9

THE EFFECT OF DOUBLING THE SOLVENT-TO-FEED RATIO ON THE ANNUAL OPERATING COSTS OF A 300,000 LB/YR. BLEACHING CLAY DE-OILING PLANT

ITEM	BASE CASE $	2 (S/F) RATIO $
1. Labor, 1 Operator, $20/hr salary, fringes and overhead	40,000	40,000
2. Electric Power, $0.075/Kwh	5,600	11,200
3. Make-Up Solvent, .7 lbs/hr., $0.70/lb.	1,000	1,000
4. Maintenance, 4% of Capital Investment	6,800	9.200
5. Taxes, 2% of Capital Investment	3,400	4,600
6. Depreciation, 10% of Capital Investment	17,000	22,900
7. Solids Disposal, $0.05/lb.	6,500	6,500
TOTAL ANNUAL COST	80,300	95,400

V. PREPARATION OF STANDARDS AND CONTROLS USED TO EVALUATE THE SOXHLET OIL ANALYSIS OF SOLID FEEDS AND RESIDUES

a. Standards

Samples of unused dry bleaching clay and vegetable oil were sent to us by a commercial client, and these were used to make the standards shown in Table A8. After a known mass of clay was added to an extraction thimble, a corresponding mass of oil was added in order to prepare standards in the range of 0, 5, 10 and 20 wt. % oil. Since all of the mixing and weighing of the sample occurred within the extraction thimble, this was thought to be an accurate method of preparation.

b. Controls

A well mixed sample of oily bleaching clay is kept in the laboratory and tested with every series of soxhlet extractions to determine the long-term precision of this technique, and to point out any immediate problems that may be encountered for a given set of extractions.

c. Bearingless Liquid Flowmeter:

A reproduction of the calibration test procedure supplied to us by the manufacturer is reporduced below:

BEARINGLESS METER CALIBRATION TEST PROCEDURE

The flow test is conducted by supplying 50 PS, 60°F water through a rotameter and through the Bearingless meter to a calibrated standpipe test tank calibrated between two contact setpoints of start and stop to the frequency counter.

The accuracy of the volumetric test vessel is ±0.5cc in 1000cc. Calibration is by filling to the adjustable upper setpoint with calibrated Beaker to nearest 0.1cc.

Meter construction is 316SS body and jet ring, glass fiber optic and epoxi rotor and optic sealpotting "O" ring is teflon. White dots on rotor are also epoxi.

d) VENDOR SUPPLIED CALIBRATION AND OPERATING SPECS

American Meter Dry Test Meter (Aluminum Case Diaphragm)

Gas Meter Selection Characteristics

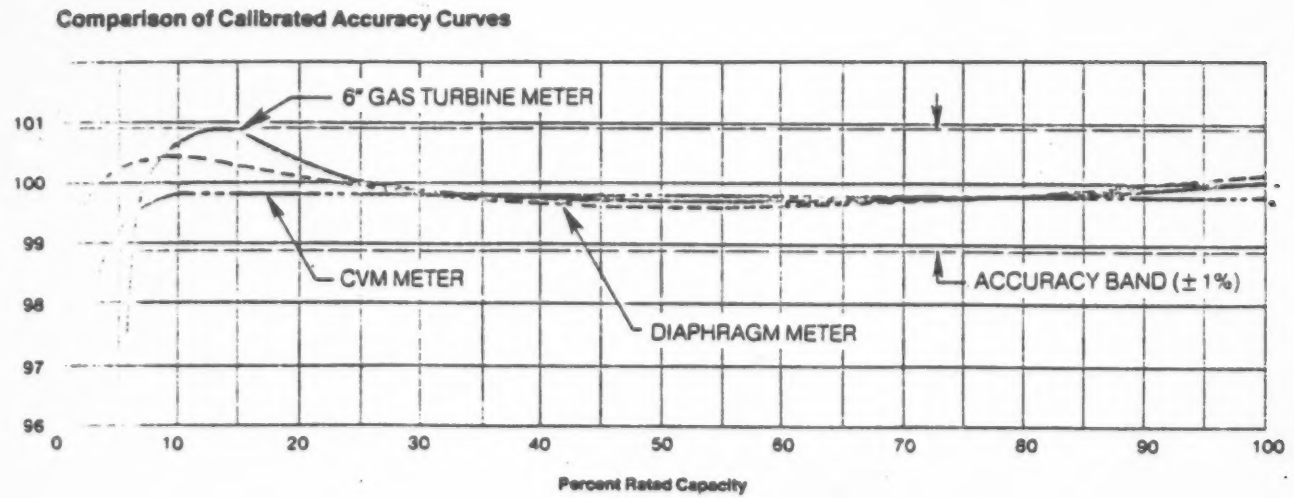
Meter Type	Maximum Operating Pressure psig	Flowing Gas Temperature °F	Influence of Condensate	Calibrated * Accuracy	Calibrated Rangeability	Straight Pipe Length in Pipe Diameters	Ambient Temperature Range °F	Installation Limitations of Meter
Aluminum-case (AL) Diaphragm	100	−30 to +140	Potential	±1	100:1	None	−30 to +140	Level
2M CVM	175	−20 to +140	None	±1	20:1	None	−20 to +140	Not Critical
CVM	1440	−20 to +140	None	±1	25:1	None	−20 to +140	Not Critical
Gas Turbine†	1440	−20 to +140	None	±1	12: 1 to 25:1	3, 4, 6, & 8 GT None · 12" GT 4 Diameters	−20 to +140	Approximate Horizontal or Vertical
Orifice	2500	−65 to +500	Potential	±1.5	3.5:1	10 to 40 Diameters	−30 to +180	Horizontal

†**Note:** *With increased operating pressure, the rangeability of the GT Meter increases above the base rangeability.*
* *See Chart on Page 4*

d) VENDOR SUPPLIED CALIBRATION AND OPERATING SPECS (continued)

American Meter Dry Test Meter (Aluminum Case Diaphragm)

COMPARISON OF CALIBRATED ACCURACY CURVES



VI. SAMPLE CUSTODY

a) All waste stream samples received by our laboratories during the time of this project were recorded in a sample log notebook, and an actual page from this book is reproduced here.

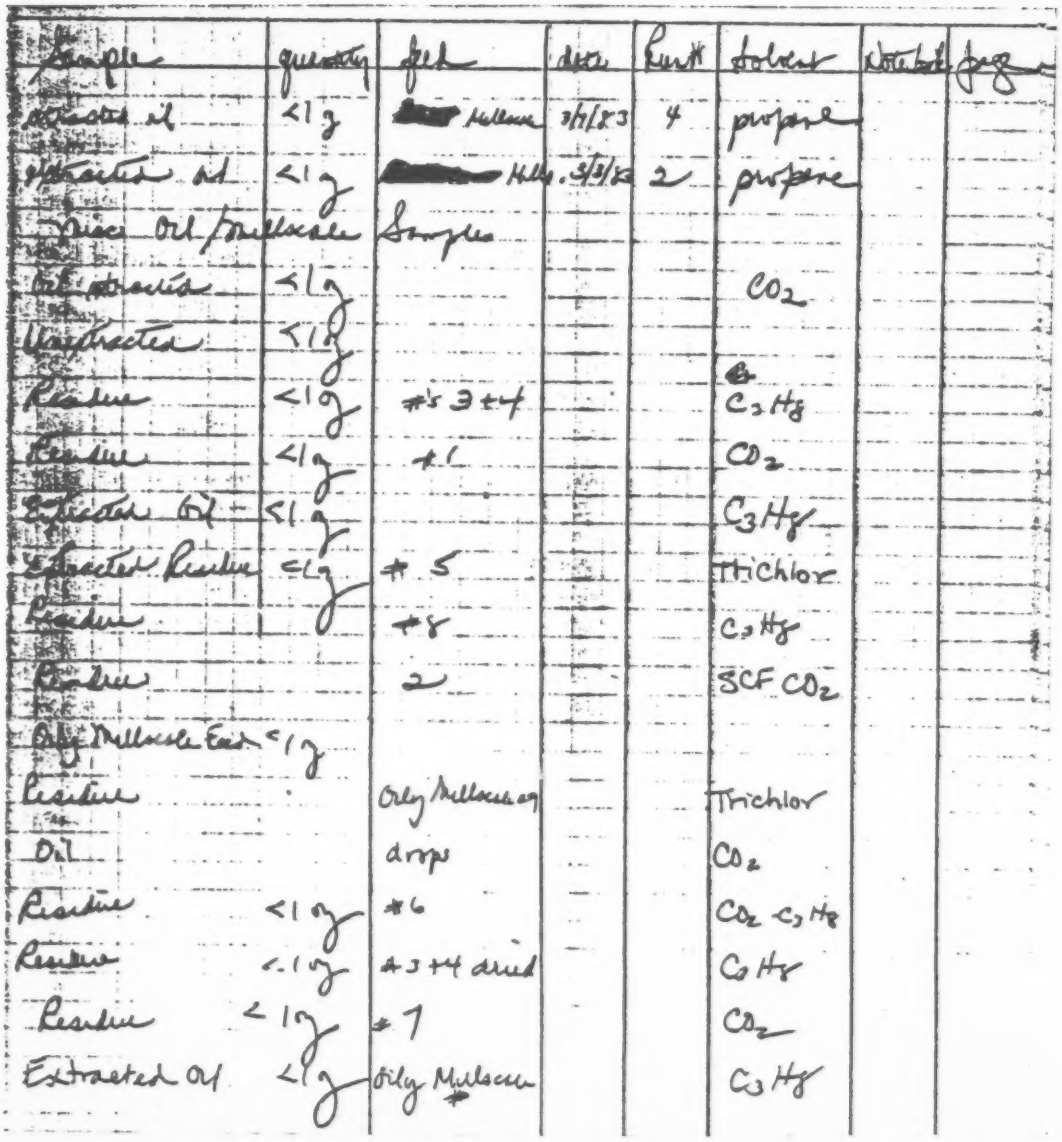
SAMPLE LOG

Bleaching Clay Samples

NUMBER	DESCRIPTION	QUANTITY	DATE RECEIVED	SAMPLE JAR FILLED
B-1	Vegetable Oil [redacted]	2-5 gal pails	3/14/83	✓ 3/18/83
B-2-A	[redacted] Silicone Oil Y126	30#	3/21/83	4/15/83
B-2-B	[redacted] Silicone Oil KOH Low Vis Dry	55#	"	4/19/83
B-2-C	[redacted] DIMETH.	48#	"	4/19/83
B-2-D	[redacted] Silicone Oil Low Filter	43#	"	4/19/83
B-3	[redacted] Vegetable Oil	1 gallon can	4/11/83	4/19/83
B-4	[redacted] Silicone Oil	1-5 gal pail	4/15/83	4/19/83
B-5	[redacted] Silicone Oil	1-5 gal pail	5/21/83	5/21/83

Note: Client names have been deleted.

b) Samples generated within our labs were also recorded into a sample log book, and a representative page is reproduced here.



Sample	quantity	field	date	Run #	Solvent	Notebook	page
Extracted oil	<1 g	[redacted] Millers	3/1/83	4	propane		
Extracted oil	<1 g	[redacted] Hills	3/3/83	2	propane		
Dried Oil/Millscale	Samples						
Oil Extracted	<1 g				CO_2		
Unextracted	<1 g						
Residue	<1 g	#'s 3 + 4			C_3H_8		
Residue	<1 g	#1			CO_2		
Extracted Oil	<1 g				C_3H_8		
Extracted Residue	<1 g	# 5			Trichlor		
Residue		#8			C_3H_8		
Residue		2			SCF CO_2		
Oily Millscale Ext	<1 g						
Residue		Oily Millscale			Trichlor		
Oil		drops			CO_2		
Residue	<1 g	#6			CO_2 C_3H_8		
Residue	<1 g	#3+4 dried			C_3H_8		
Residue	<1 g	#7			CO_2		
Extracted Oil	<1 g	Oily Millscale #			C_3H_8		

Note: Client names have been deleted.